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Long-term Acid Deposition Effects on Soil and Water Chemistry in the Noland Divide Watershed, Great Smoky Mountains National Park, USA

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To the Graduate Council:

I am submitting herewith a dissertation written by Meijun Cai entitled "Long-term Acid Deposition Effects on Soil and Water Chemistry in the Noland Divide Watershed, Great Smoky Mountains National Park, USA." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Civil Engineering.

John S. Schwartz, Major Professor

We have read this dissertation and recommend its acceptance:

R. Bruce Robinson, Randall W. Gentry, Amy M. Johnson

Accepted for the Council:
Dixie L. Thompson

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

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A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Meijun Cai
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Abstract

Impacts of long-term acid deposition on soil and water chemistry are of particular concern in the Great Smoky Mountains National Park (GRSM), receiving some of the highest acid deposition rates in the eastern United States and limited by inadequate acid buffering capacity. In the GRSM, the Noland Divide watershed (NDW) has been monitored since 1991 for water chemistries of precipitation, throughfall, soil, and stream. The impacts of long-term acidic deposition on stream water quality in the NDW were investigated through: 1) development of an ion input-output budget; 2) analysis of trends and seasonal patterns for major ions; 3) comparison of net export rates between baseflow and stormflow periods; and 4) characterization of soil chemistry and transport properties for various potential acid deposition scenarios. Between 1991 and 2006, throughfall deposition remained unchanged and consisted of 1,735 eq ha^{-1} yr^{-1} of SO_4^{2-}, 863 eq ha^{-1} yr^{-1} of NO_3^-, and 284 eq ha^{-1} yr^{-1} of NH_4^+. Net retention of sulfate was estimated at 61% being controlled by soil adsorption, and inorganic nitrogen was retained at 32% presumably due to plant uptake. Nitrogen retention increased by 44.30 eq ha^{-1} yr^{-1} over the study period. Besides deposition, soil acidity was increased by nitrification and precipitation-driven desorption of previously accumulated sulfate. To neutralize soil acidity, Ca^{2+}, Mg^{2+} and Na^+ were depleted from NDW by 77, 46 and 66 eq ha^{-1} yr^{-1}, respectively. Due to the continuous addition of acidity, base saturation in soil was reduced to 4% at present. Mobilization of aluminum and other metals (Mn and Zn) may be enhanced by these geochemical processes, potentially causing toxic conditions to fish and other biota in the GRSM streams. Impacts of acidic deposition on streams were confirmed by measured stream pH below 6 and acid neutralizing capacity below 0.01 meq L^{-1}. During stormflows pH and ANC depressions occurred primarily due to increases in sulfate transport, leading to episodic acidification events. This study provides new information on

hydrological and biogeochemical processes that regulate stream acidification events in the southern Appalachian region, supporting improved management strategies for GRSM streams.

Table of Contents

List of Tables

List of Figures

CHAPTER 1 INTRODUCTION

Acid deposition, resulting mainly from fossil combustion and vehicles emission, has had deleterious effects on terrestrial and aquatic ecosystems (Herlihy et al., 1991). Adverse acidification impacts to surface water and soil include reduction of the acid neutralization capacity (ANC), depression of surface water pH, depletion of base cations, and increase of inorganic aluminum in water (Driscoll et al., 2001). Indirect impacts include the accumulation of sulfur and nitrogen in the soils, which may delay the watershed recovery from acidification in the future (Driscoll et al., 2003). Such changes in soil and water acid-base chemistry can affect the ecological health of terrestrial forests by limiting the nutrient supply and aquatic organisms by exposing them to toxic chemicals (Baker et al., 1990; DeHayes et al., 1999; McLaughlin and Wimmer, 1999). Adverse impacts of acid deposition to soil and water chemistry have been observed throughout the southern Appalachian region of the eastern United States (McLaughlin et al., 1993; Sullivan et al., 2007). The potential for these impacts addresses the importance of studying the change of water and soil chemistry in order to identify and quantity the effects of acid deposition.

Assessment of water and soil acidification in the Great Smoky Mountains National Park (GRSM) of southern Appalachians is especially important since acid deposition in the GRSM has caused adverse impacts on water quality, soils and some sensitive species in aquatic ecosystem (Silsbee and Larson, 1982; Cook et al., 1994). With respect to water quality, a study of 90 GRSM stream sites found that 59% of those sites have ANC less than 50 $\mu eq\ L^{-1}$ and 21% has a base flow pH below 6.0 (Robinson et al., 2008). It is believed that episodic and chronic acidifications are the major factors for the loss of brook trout within the GRSM, especial the

extirpation of brook trout populations in six GRSM headwater streams in 1990s (Deyton et al., 2009; Neff et al., 2009; Moore, *unpublished data*).

High-elevation watersheds are particularly susceptible to acid deposition as they receive four- to sixfold greater amount of acid deposition than that in low-elevation watersheds in GRSM (Weathers et al., 2006). Base-poor geology and relatively thin soils in high-elevation watersheds offer limited buffer capacity (Shubzda et al., 1995). As one of the high-elevation watersheds in the GRSM, Noland Divide Watershed (NDW) is selected as a monitoring site to characterize acid deposition rates and effects to this ecosystem. In order to evaluate the impacts of acid deposition in the NDW, water quality in this watershed was studied as part of the Integrated Forest Study (IFS) monitoring sites from 1985 through 1991, and NDW has been part of the Inventory and Monitoring (I&M) program of the GRSM since 1991 to the present (Johnson and Lindberg, 1992). However, assessments of stream and soil acidification in the NDW have been limited to early surveies in the late 1980s or short-term monitoring data collected during 1990s (van Miegroet et al., 2001; Barker et al., 2002). Most studies focused on one chemical or chemistry in one medium, water or soil (Nodvin et al., 1995; Tewksbury and van Miegroet, 2007). There is a critical need for a comprehensive analysis in order to provide a sufficient understanding of watershed acidification processes. The extensive data set from the NDW can be used to evaluate the watershed processes and acidification.

Given the concern of GRSM natural resource managers over the potential effects of acid deposition, the objectives of this study were to investigate the soil and stream water chemical response to long-term acid deposition in the NDW and to investigate relationships of watershed response to acidic deposition. In addition, an objective was to attempt prediction of potential outcomes if reduced deposition loads of sulfur and nitrogen would occur in the future. In order to

meet these general objectives, a 17-year monitoring dataset (1991-2007) of water chemistry and one year soil chemistry data, obtained from laboratory and field experiments, were utilized to analyze ion budgets, temporal trends of acid ions in deposition and stream export, episodic acidification, soil characterization and soil drainage chemistry in future. This dissertation is organized in chapters as a journal paper or manuscript draft from Chapters 3 to 7. The study area, including site location and motoring stations is present in Chapter 2 and it is common for all chapters. In conclusion, Chapter 8 summarizes the findings from this dissertation and recommends future research.

Chapter 3: This chapter is the first comprehensive assessment of acidic deposition, stream export and soil solution. The goal of this chapter was to quantify ion input and output budgets in order to investigate the key acidification processes within this watershed. This chapter was based on 16-year water chemistry data monitored in the NDW from 1991 to 2006. It set out to answer fundamental questions such as: how much annual deposition and export of acid ions occurs; what are the dominant ions, and what is the change of ion after passing through this watershed. Based on the calculation of ion budget, the possible biogeochemical processes that control changes in ion mass were investigated. In addition to calculation of ion budget, the correlation of deposition and stream water chemistry was examined to identify the effects of deposition to stream water quality. Results from this chapter have been published in *Water, Air and Soil Pollution* (2009).

Chapter 4: Since the implementation of Clean Air Act, the deposition loads of sulfur and nitrogen are expected to decline and the watershed is expected to show signs of recovery. The goal of the fourth chapter is to document changes in the deposition of sulfur and nitrogen over time and to evaluate changes in stream chemistry to determine if the system is recovering from long-term acidic deposition. Deposition and stream water chemistry monitored during 1992 to

2007 were utilized to investigate the time trend of the acid anions (nitrate, sulfate), pH and ANC. Temperature, vegetation and hydrology are changing seasonally and may affect the watershed export of acid anions. The seasonal variation of acid anions in deposition and stream water were explored in order to evaluate variability of pH, ANC, SO_4^{2-} and NO_3^-, and provide evidence of SO_4^{2-} and N fate and transport in watersheds impacted by acid deposition.

Chapter 5: Episodic acidification during stormflow is a greater concern than chronic acidification because episodic acidification is more widespread in US and aquatic life is more vulnerable to episodic acid exposure. Scientists usually attribute surface water episodic acidification to the elevation of acid anions and depression of base cations during storm event. In order to investigate the chemical changes caused by episodic acidification in the NDW, stream acid anions and base cations were compared during baseflow and stormflow. This chapter studies how and to what degree the stream flow affects the water chemistry variability during episodic stormflow and baseflow.

Chapter 6: Long-term acid deposition has the potential to reduce the base cation pool and accumulate sulfate reducing the soil buffering capacity to acid addition. Chemical properties of soil, especially the base saturation in the NDW was unknown. The goal of this chapter was to characterize soil chemistry studying the effects of long-term acid deposition in soil. In addition, adsorption and desorption reactions of sulfate on soil, potential nitrogen mineralization, and nitrification rates were experimentally measured. The soil chemistry data provided could be employed in biogeochemical modeling of this watershed. A revised version of this chapter has been submitted for review to *Journal of Environmental Quality*.

Chapter 7: As soil in the NDW has low base saturation, the behavior of watershed recovery from acidification in response to reduced acid deposition load is particularly problematic. The

purpose of this chapter was to investigate the soil drainage chemistry in response to simulated acid deposition, which had reduced loads of sulfur and nitrogen. This work was accomplished through laboratory column and field soil leaching experiments to examine the soil effluent with different acid deposition loads. Through this work, this chapter answered the following questions: whether and how the watershed can recover from acidification if acid deposition loads are reduced; which processes are determining watershed acidification; what impacts will be caused by water flow rate to drainage chemistry. Breakthrough curves of soil drainage chemistry were simulated to understand the dynamics of soil processes associated with acidification.

CHAPTER 2 STUDY AREA

The Noland Divide Watershed (NDW), a high-elevation (1,680 - 1,920 m MSL) 17.4 ha GRSM watershed, served as the study area (Fig. 2-1). Two perennial first-order streams (NE and SW streams) drain the study area headwaters and merge downstream as Noland Creek. Measured by a meteorological station located 100 m below the study area, mean annual air temperature was 8.5^{o}C, ranging from -2^{o}C in January to +18^{o}C in July (Shanks, 1954; van Miegroet et al., 2001). The frost-free period occurs from May through September. Annual precipitation ranges from 200 to 300 cm generally, 10% of which consists of snow (Johnson et al., 1991; Johnson and Lindberg, 1992; Shubzda et al., 1995).

Overstory forest in the NDW is dominated by red spruce (*Pices rubens,* Sarg) accounting for 77% by area, interspersed with patches of yellow birch (*Betula alleghaniensis*) accounting for 19% by area (Barker et al., 2002). Fraser fir (*Abies fraseri,* Poir) once dominated this watershed, but now only accounts for about 2.5% of the area. Red spruce becomes relatively more abundant with increasing elevation, while yellow birch declines.

NDW soils are shallow Inceptisols with spodic characteristics classified as Dystrochrepts or Haplumbrepts, consisting of silt loam to sandy loam texture (McCracken et al., 1962; van Miegroet et al., 1993). Soil layers were described by Johnson and Lindberg (1992) consisting of 4-cm thick Oi + Oe horizon of needles and leaves; 4-cm thick Oa horizon of mucky humus; 8-cm thick A horizon of dark, reddish-brown, mucky loam; 27-cm thick Bw horizon of dark brown, sandy loam; 35-cm thick Cb horizon of dark, yellowish-brown loam; and 20-cm thick C horizon of olive-brown, loamy sand. The geology in this area of the park was previously assigned to the Thunderhead Formation (King et al., 1968) but upon a more recent and thorough geologic survey

has been designated as being part of the Copperhill Formation which is stratigraphically higher than the Thunderhead Formation (USGS, 2005). Both of these formations are predominately sandstone and are in the Great Smoky Group with the major distinction between the two being the presence of the intervening slaty rock in the Thunderhead Formation (USGS, 2005).

The NDW was equipped with five monitoring stations to measure atmospheric deposition (wet deposition and throughfall stations), soil water (lysimeter station), and SW and NE stream stations (Fig. 2-1). Water quality samples were collected weekly from 1991 to 2000 and then biweekly since that time at deposition and stream stations, and monthly at the soil station. Stream stations were equipped with sondes and stage recorders collecting pH, temperature, conductivity, and flow at 15-minute intervals. The NDW was selected for study because: 1) of its high elevation location where acidic deposition is known to occur at greater rates than lower elevations; and 2) its proximity within 2 km of the National Atmospheric Deposition Program site at Clingman's Dome (NADP, 2006).

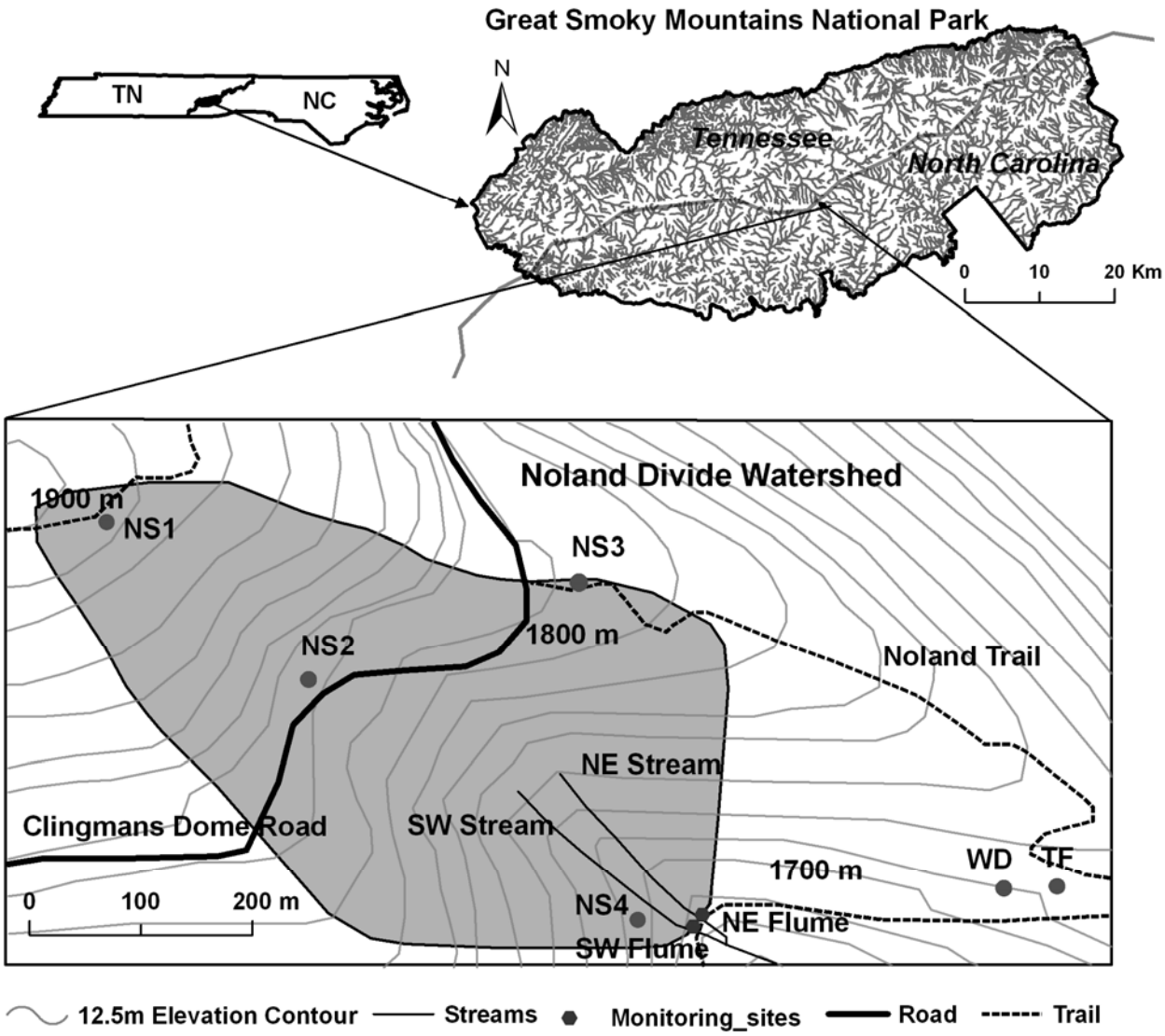

Fig. 2-1. Location of the Noland Divide Watershed (NDW) in the Great Smoky Mountains National Park, Tennessee (GRSM), five long-term monitoring stations and four soil sampling sites (Lat 35°34'N, Long 83°29'W). Monitoring stations included: wet deposition (WD), throughfall (TF), soil lysimeters adjacent to TF station, and southwest (SW) and northeast (NE) stream flumes. NS1, NS2, NS3 and NS4 are four sites to take soil samples used in this dissertation. In addition, the field soil leaching experiment was conducted in NS4 site.

CHAPTER 3 LONG-TERM EFFECTS OF ACIDIC DEPOSITION ON WATER QUALITY IN A HIGH-ELEVATION GREAT SMOKY MOUNTAINS NATIONAL PARK WATERSHED: USE OF AN ION INPUT-OUTPUT BUDGET

This chapter is a slightly revised version of a paper with the same title accepted for the *Water, Air and Soil Pollution* by Meijun Cai, John S. Schwartz, R. Bruce Robinson, Stephen E. Moore, and Matt A. Kulp.

ABSTRACT

Impacts from acidic deposition on stream water quality in the Great Smoky Mountains National Park (GRSM) have long been reported, however a better understanding of the biogeochemical processes that regulate stream acidification is needed for resource management. Water quality monitoring of Noland Divide Watershed (NDW), a high-elevation watershed in the GRSM, was used to generate an ion input-output budget in order to evaluate what processes have influenced stream pH and acid neutralizing capacity (ANC) over the long term. NDW was equipped with wet deposition, throughfall, soil lysimeters, and stream collection stations, and monitoring began in 1991 and continues to the present. Using data from 1991-2006 this study found annual deposition fluxes of SO_4^{2-} and NO_3^- averaged 1,735 and 863 eq ha^{-1} yr^{-1}, respectively. Data indicated that 61% of the net SO_4^{2-} entering the watershed was retained, suggesting soil adsorption dominates as a biogeochemical process. Although, net SO_4^{2-} retention was observed, SO_4^{2-} appeared to move rapidly through NDW during large precipitation events causing stream acidification, as evidenced by significant inverse correlations between biweekly throughfall SO_4^{2-} flux and stream event pH and ANC. Nitrogen uptake by forest vegetation and nitrification play key roles in regulating NO_3^- export to the stream as observed by 32% retention of net inorganic nitrogen, and 96% of NH_4^+ input was converted to NO_3^- in the uppermost soil horizon. Net export of base cations (Ca^{2+}, Mg^{2+}, Na^+) was observed, and apparently moderates

stream acidification. In contrast, 71% of net K^+ input was retained, which is likely due to forest vegetation uptake. Net export of Ca^{2+} was 867 eq ha^{-1} yr^{-1} compared to net throughfall of 790 eq ha^{-1} yr^{-1}. Long-term cation depletion from the NDW soils could limit recovery potential in stream water quality. Findings from this NDW study suggest that future stream acidification conditions in high-elevation GRSM watersheds are dependent on interrelated biogeochemical processes and precipitation patterns, illustrating the need to better understanding potential impacts of climate variability on stream water quality.

Key Words: stream acidification, acidic deposition; biogeochemical processes; watershed input-output budgets, water quality, Great Smoky Mountains, critical loads.

INTRODUCTION

Impacts of long-term acidic deposition on stream water quality are a major concern to resource managers of the Great Smoky Mountains National Park (GRSM). It has been known for decades that atmospheric deposition of SO_4^{2-} and NO_3^- from coal-fired power plants, vehicles and other sources can cause stream acidification in Appalachian regions with base-poor bedrock (Driscoll et al., 1980, Herlihy et al., 1991; Wigington et al., 1996). Stream acidification in the GRSM was initially observed in the 1980s by Johnson and Lindberg (1992) and Cook et al., (1994). During this period, acidic deposition was characterized at the Noland Divide Watershed (NDW) in the GRSM as part of the Integrated Forest Study (IFS), a North American and European program to examine its effects on forest nutrient cycles (Lindberg and Lovett, 1992). After the IFS, GRSM resource managers initiated a long-term study utilizing the NDW site to further investigate impacts of acidic deposition on high-elevation forested watersheds and stream

acidification. In 1991, the NDW was equipped with precipitation, throughfall, soil lysimeters, and stream monitoring stations, designed to characterize and assess deposition, soil, and stream water chemistries over time. In this study, analysis focused on estimating ion fluxes for annual input-output budgets utilizing the NDW monitoring data from 1991 through 2006.

Input-output budgets have been widely used to study acidification impacts on streams from acidic deposition (Löfgren and Kvarnäs, 1995; Mitchell et al., 1996; Driscoll et al., 1998; Castro and Morgan, 2000; Watmough et al., 2005). Key biogeochemical processes operating in watersheds can be inferred from ion input-output budgets. For example, Dow and DeWalle (1997) found one watershed retained 58% of its net SO_4^{2-} atmospheric inputs compared to four other mid-Atlantic watersheds in which stream SO_4^{2-} was in balance or was exported in greater mass than atmospheric inputs. Sulfate retention has mostly been attributed to soil adsorption (Evans et al., 1997; King et al., 2006). Palmer et al. (2004) observed declines in atmospheric deposition of SO_4^{2-} but not stream concentrations at Hubbard Brook Experimental Forest (HBEF) and suggested sulfate desorption from soils as one possible process for the excess SO_4^{2-} export. Similarly in a western Maryland study, Castro and Morgan (2000) found net SO_4^{2-} to be exported 1.6 times greater than through atmospheric inputs. Sulfate mass budgets are mostly dependent on soil adsorption-desorption, which is affected by soil type, SO_4^{2-} input concentration, soil water pH, and dissolved organic carbon (Gobran et al., 1998). In addition, net export of SO_4^{2-} may be generated from net organic S mineralization and weathering of S-bearing rock (Mitchell et al., 2001).

Watershed retention of nitrogen is dependent on forest vegetation uptake, nitrification rates in the upper soil horizon, soil properties and hydrological flow paths, where both net export and retention have been reported from input-output budgets (Williard et al., 1997; Shibata et al., 1998;

Farrell et al., 2001). An analysis of the NDW data from 1993 through 1997 found about 50% of net NO_3^- input was exported annually, suggesting soils were N-saturated (van Miegroet et al., 2001; Barker et al., 2002). In contrast, NO_3^- was mostly retained in study watersheds in the northeastern United States and Canada (Mitchell et al., 1996; Dow and DeWalle, 1997; Yanni et al., 2000).

Prolonged acidic deposition has been suggested as one possible cause for observed net declines in soil exchangeable base cations, primarily Ca^{2+} (Fernandez et al., 2003; Lawrence, 2002; Groffman et al., 2006). Several studies have reported net base cation export from watersheds including Ca^{2+}, Mg^{2+}, and Na^+ (Dambrine et al., 1998; Castro and Morgan, 2000). Castro and Morgan (2000) found K^+ to be exported, whereas Farrell et al. (2001) found K^+ to be retained, assuming due to vegetative uptake. From 1985 to 1988 at the HBEF, Palmer et al. (2004) found base cations declined in streams and Ca^{2+} declined in soil water, suggesting the occurrence of soil cation depletion.

Results from existing input-output budgets illustrate ion fluxes in watersheds are variable, dependent on geology, forest vegetation, soils, and climate (Deviney et al., 2006; Sullivan et al., 2007; Deyton et al., 2009). These environmental factors control stream acidification response through biogeochemical processes that regulate ion export in watersheds (Mitchell et al., 2001; Palmer et al., 2004; Watmough et al., 2005). Quantifying net ion inputs and outputs in a watershed provides the necessary validation data for biogeochemical model development, which model use can provide further insight to what processes control stream acidification response from acidic deposition (Sullivan et al., 2004; Wright et al., 2006; Sullivan et al., 2008). Importance of this GRSM research is emphasized by the fact that the native southern brook trout has been extirpated in six watersheds while other watersheds maintain viable populations

(*unpublished data*, S. Moore). With the support of a process-based model and toxicologically-relevant targets defined by Neff et al. (2009), critical loads can be estimated in order to guide emission reductions to allow for native brook trout recovery.

Within the NDW study goals, objectives of this article were to: 1) investigate long-term changes in water chemistry (1991-2006) among watershed hydrologic system compartments including precipitation, throughfall, soil water, and streams; 2) complete an ion input-output budget, and estimate long-term net ion fluxes for retention or export; and 3) statistically investigate relationships between acidic deposition and stream acidification by measured event ion concentrations. The focus of this article was on improving our understanding what possible biogeochemical processes influence fate and transport of atmospheric acid pollutants in GRSM high-elevation watersheds.

METHODS

Study Design

In order to meet the study objectives, net ion inputs and exports were computed from mean annual ion fluxes over the long-term in the NDW. A watershed biogeochemical framework for element sources, sinks and exports that supports the study design is shown in Fig. 3-1. This framework identifies atmospheric deposition as the key acid pollutant source, the interception of water with the forest canopy and soil matrix as a source/sink, and stream flow as the major system outlet for element export. Monitoring of these watershed hydrologic system compartments provide the essential information to compute ion net flux balances of input (atmospheric deposition) and output (stream export), characterizing whether an ion was retained or depleted from the NDW. Retention includes chemical transformations. Within a watershed ion

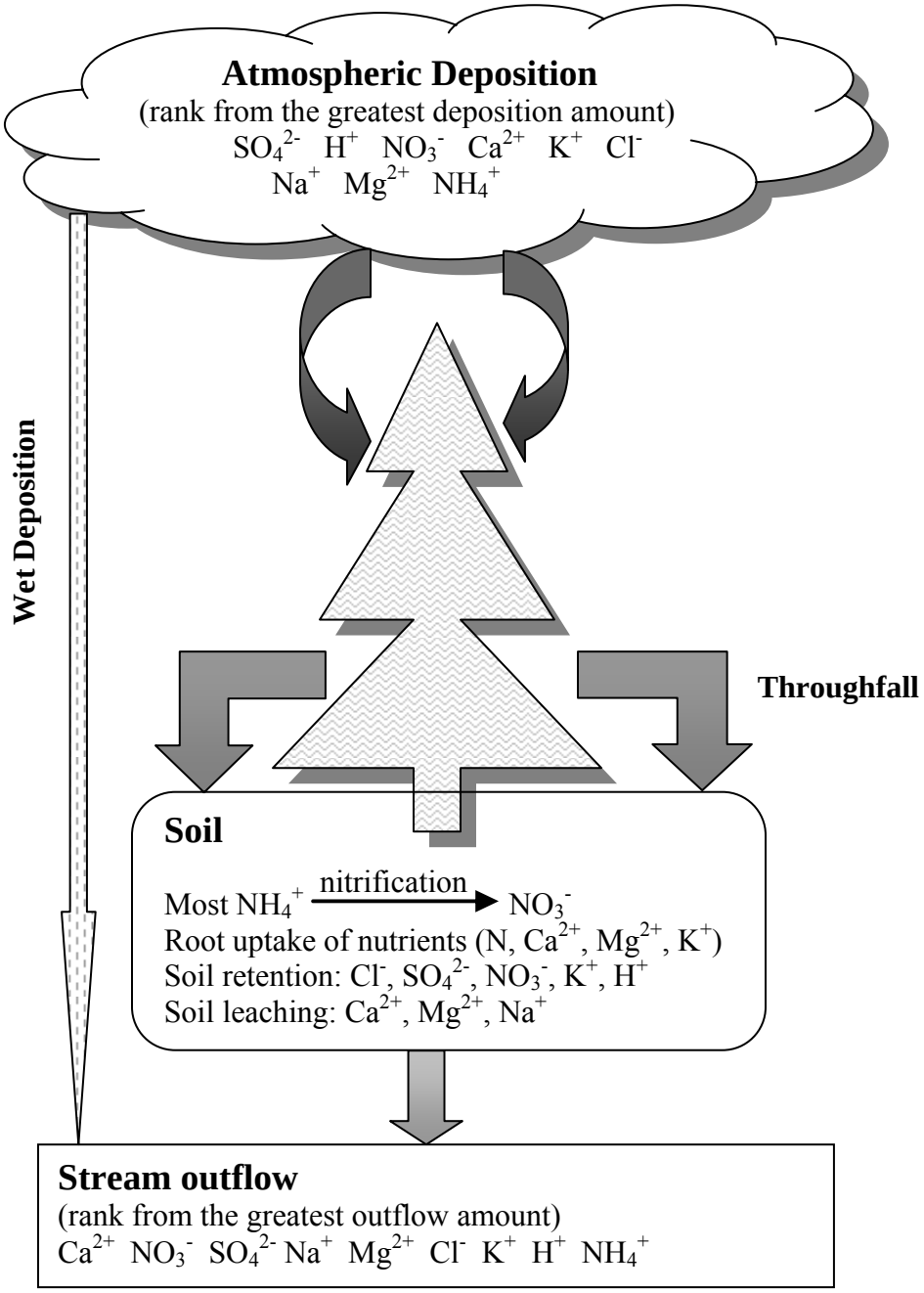

Fig. 3-1. Conceptual framework for ion transport among watershed hydrologic system compartments, including: atmospheric deposition, forest canopy and soil matrix, shallow groundwater, and headwater streams. Ions per hydrologic compartment listed in order of flux for the NDW study site.

input-output budget approach, hydrochemical processes associated with net ion retention or depletion could potentially be identified.

The study consisted of the following analyses: 1) mean annual water and ion fluxes were computed to quantify net input and output in NDW, and estimate net retention and depletion; 2) changes in annual volume-weighted mean concentrations were examined among the watershed hydrologic system compartments from deposition through the canopy to soil water, through the three soil horizons (A, Bw, and Cb), and from soil water to stream water; and 3) measured precipitation and event SO_4^{2-} and NO_3^- concentrations for wet deposition and throughfall were correlated with stream pH and acid neutralizing capacity (ANC).

Field Data Collection and Laboratory Analysis

Wet deposition samples: Wet deposition was collected at an open site (without forest cover) using a rainfall collector with a precipitation-triggered cover. Deposition water was collected and weighed biweekly to obtain a precipitation volume, computed by use of water specific weight.

Throughfall samples: During frost-free periods, throughfall was collected by ten covered collector buckets mounted with 90-mm diameter funnels to minimize evaporation, and during the frost season two open 5-gal collector buckets were used to composite a sample. Use of covered throughfall collectors began in 2005, prior to which open collector buckets were used year around. Throughfall volumes were calculated by the same method as wet deposition samples, in which sample water was weighed from all collectors biweekly. Stem flow was not collected based on previous studies, which showed this flux to be less than 5% of throughfall in coniferous forests (Ulrich, 1983).

Soil water samples: Soil water samples were collected monthly by four ceramic suction lysimeters at each of three different soil depths, and analyzed as single composite samples per

soil layer. Shallowest depth lysimeters were placed in the A horizon, intermediate depth lysimeters were placed in the Bw horizon, and the deepest lysimeters were placed in the Cb horizon. Lysimeters were installed in the same location as the throughfall collectors (Fig. 2-1).

Stream water samples: Grab samples were collected from the SW and NE streams weekly from 1991-2000 and biweekly since 2001. Most samples were collected during baseflow conditions, and no effort was made to collect only baseflow samples. Each stream was also equipped with water quality sondes recording pH, conductivity and temperature. Float-type stage recorders were installed in stilling wells on 3.0-ft H flumes, in which discharge was calculated from flow depth according to standard H-flume tables in USDA-ARS (1979) and periodically verified. Water quality and stage data were recorded every 15 minutes on a Campbell CR10 data logger.

Laboratory Analysis: All water samples were transported to the University of Tennessee Water Quality Laboratory within 4 hours and analyzed for pH, conductivity, and ANC utilizing an autotitrator within 24 hours. Samples in holding were kept cooled at 4^{o}C. Samples were filtered by a 0.4-μm membrane and separated into two bottles for analysis of SO_4^{2-}, NO_3^-, Cl^-, and NH_4^+ by ion chromatography; and Ca^{2+}, Mg^{2+}, K^+, Na^+ by atomic absorption spectrometry (1991-1993, 1998-2003) and inductively-coupled plasma spectrometry (2003-2006). From 1993 to 1998, Na^+ and K^+ were measured by ion chromatography, but Ca^{2+} and Mg^{2+} were not measured. Measurement of ANC for wet deposition, throughfall, and soil water began in 2005. All samples met quality criteria set forth in a quality assurance/quality control (QA/QC) program, which included sample spikes, replicates, blanks and U.S. Geological Survey known samples; in addition to adherence to analytical equipment maintenance. Sample and QA/QC data can be obtained from STORET (2008).

Water Volume and Ion Flux Calculations

Water volumes and ion fluxes were computed annually by Julian year, and averaged over the study period. Annual water volume balances were estimated by the difference between throughfall and total stream flow, reported in units of mm yr^{-1} (water loss = throughfall – total stream outflow). The water loss due to direct evaporation above canopy cannot be accounted by throughfall volume, and is not considered in this study. Annual throughfall was computed by converting each volume collected biweekly to a depth (mm) based on the total surface area of the collection funnels, and summing each biweekly measurement to equate to an annual total. Annual volume for total stream outflow as NDW water export was computed by summing measured volumetric discharges (m^3 s^{-1}) per 15-minute increments for both SW and NE streams, combining these individual stream annual volumes (m^3), dividing total annual volume by total watershed area (17.4 ha), and converting units to obtain estimates in mm yr^{-1}. Discharge estimates for SW and NE streams in mm yr^{-1} were computed by relative portions of total annual volumetric discharges per stream. Water loss was that hydrologic portion due to evapotranspiration and groundwater flow bypassing the NDW study outlet location, and is seasonally variable (Cai et al., 2009).

In order to generate an ion input-output budget for the NDW, net ion retention or depletion were estimated as the difference between throughfall (TF) and stream export, reported in mean annual flux units of eq ha^{-1} yr^{-1} (retention/depletion = TF – stream export). Annual ion fluxes (eq ha^{-1} yr^{-1}) for throughfall and wet deposition were computed by multiplying biweekly measurements of ion concentrations and total collector volume, dividing by the ratio of total collector funnel area to total watershed area (ha), and summing biweekly flux estimates per Julian year periods. Dry and cloud deposition generally represented that portion computed by the

difference between throughfall and wet deposition; although some estimation error could be caused due to the interception of canopy to these elements. Ion export per stream was calculated by multiplying the biweekly chemical concentrations by the biweekly discharge volumes over that period, and summed per Julian year to obtain an annual flux. Annual total stream flux export was computed by summing eq yr^{-1} for both SW and NE streams, divided by the total NDW drainage area of 17.4 ha. Using mean net fluxes, retention represented a positive difference between TF and stream export, whereas net depletion represented a negative difference.

Statistical Analysis of Chemistry among Deposition, Soil, and Stream Waters

Statistical analysis of water chemistry among watershed hydrologic system compartments included: 1) analysis of variance (ANOVA) multiple comparison procedure to compare annual volume-weighted mean concentrations among compartments; and 2) a Kendall's τ-b correlation analysis of stream pH, ANC, SO_4^{2-} and NO_3^- with precipitation volume and SO_4^{2-}, NO_3^-, NH_4^+, and inorganic N ($NO_3^- + NH_4^+$) deposition biweekly event concentrations. Hydrologic system compartments were: wet deposition, throughfall, soil water in A, Bw, and Cb horizons, and SW stream.

Annual volume-weighted mean concentrations per hydrologic system compartment were computed by annual ion fluxes dividing by annual water volume, and averaged for the 16-year monitoring period to obtain compartment means. Annual volume-weighted concentrations were compared among compartments using an ANOVA Tukey's HSD mean separation procedure (Hayter, 1984). Significance groupings of annual volume-weighted mean concentration differences were indicated by superscript letters, e.g., A, B, C, etc. ($p \leq 0.05$). If the data did not share the same letter, it indicates there was a significant difference between those compartments. Statistical analysis was performed with JMP® v.6.0.2 (JMP, 2005). In order to identify potential

relationships between stream acidification and acidic deposition, the Kendall rank correlation analysis was used. The SW stream was chosen only for the correlation analysis not to duplicate results. Water chemistries between the NE and SW streams were not statistically different based on pH, ANC, NO_3^-, and SO_4^{2-} biweekly event concentrations (Table 3-1). The Kendall's τ-b correlation analysis was performed with SPSS v.15.0 using a significance $p \leq 0.05$ (SPSS, 2006).

RESULTS

Watershed Budgets for Water and Ion Fluxes

From late 1991 to 2006, NDW received a mean annual rainfall of 1,918 mm yr^{-1} at the open site, and throughfall of 2,175 mm yr^{-1} (Table 3-2). Throughfall was greater than rainfall precipitation by 257 mm yr^{-1} accounting for cloud and fog precipitation. Annual mean stream discharge from NDW totaled 1,714 mm yr^{-1}, where the NE stream exported 70 mm more water than the SW stream on an annual mean basis. Annual discharge was approximately 79% of throughfall deposition. The remaining 21% was assumed loss mostly to surface evapotranspiration and minor export of groundwater (Cai et al., 2009).

Annual flux input as throughfall of SO_4^{2-} averaged 1,735 eq ha^{-1} yr^{-1}, and it was greatest among the acidic anions followed by NO_3^- that averaged 863 eq ha^{-1} yr^{-1} (Fig. 3-2). Annual volume-weighted mean concentrations for SO_4^{2-} and NO_3^- throughfall, the highest among

Table 3-1. Kendall's rank correlation (τ-b) analysis for SW and NE stream pH, ANC, NO_3^-, and SO_4^{2-} biweekly event concentrations.

Statistic	pH	ANC	NO_3^-	SO_4^{2-}
τ-b	0.57	0.53	0.51	0.55
p	< 0.01	< 0.01	< 0.01	< 0.01
N	601	596	601	601

Table 3-2. Mean annual water (mm yr^{-1}) and ion fluxes (eq ha^{-1} yr^{-1}) for measured NDW inputs and exports from 1991 to 2006. Hydrology balance (TF - total stream export) reported as retention represents non-stream export. Percent retention equals retention/TF×100%.

	Water	Cl^-	SO_4^{2-}	$NO_3^- + NH_4^+$	NO_3^-	NH_4^+	H^+	Ca^{2+}	Mg^{2+}	K^+	Na^+
WD	1,918	205	483	432	210	222	480	144	31	168	122
TF	2,175	572	1,735	1,146	863	284	1,503	790	284	629	377
SW	821	126	250	331	327	4	17	391	152	69	205
NE	893	180	421	450	444	7	38	476	179	114	238
Total Stream	1,714	306	671	782	771	11	55	867	330	182	443
Retention	461	267	1,064	365	92	273	1,448	-77	-46	447	-66
% Retention	21 *	47	61	32	11	96	96	-10	-16	71	-18

WD = wet deposition; TF = throughfall; SW = southwest stream; NE = northeast stream; and Total Stream = sum of SW and NE.

* % Retention of water accounted as evapotranspiration, and verified by model simulations using WinHSPF (Cai et al., 2009).

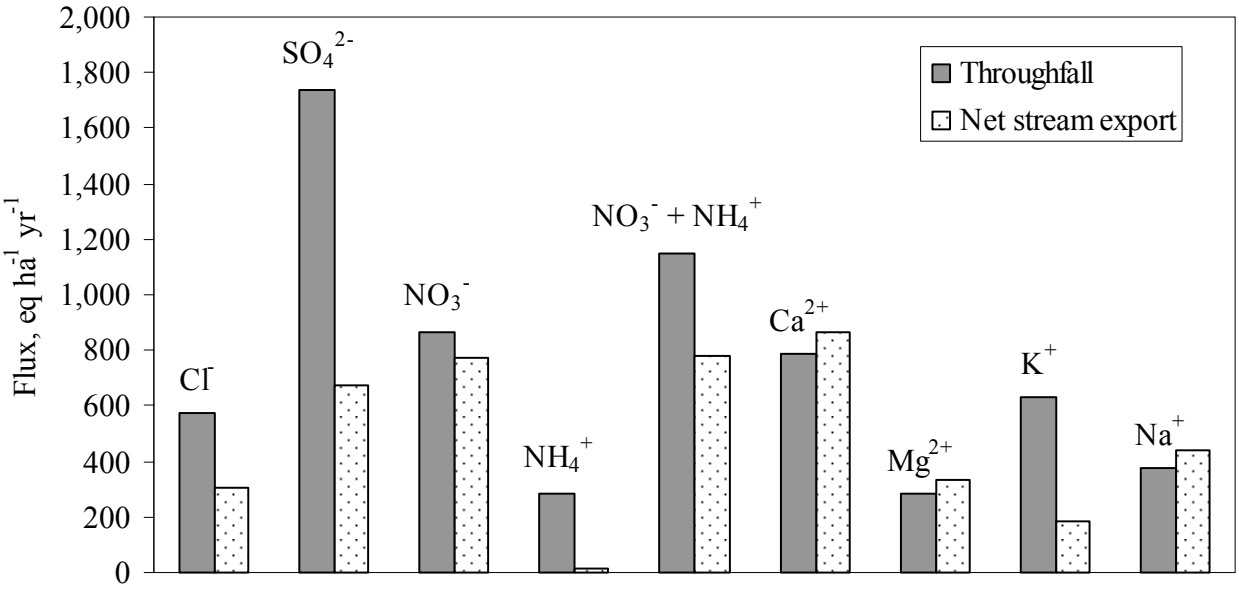

Fig. 3-2. Mean annual fluxes in eq ha^{-1} yr^{-1} for throughfall and stream net export in NDW from 1991 to 2006 for major anions and cations.

the anions measured were 81.8 μeq L^{-1} and 38.8 μeq L^{-1}, respectively (Table 3-3). Elevated concentrations of these two acid anions coincide with high proton concentrations as observed by the mean annual pH of 4.7 for wet deposition and 4.3 for throughfall. Also, mean annual ANC was –7.2 μeq L^{-1} for wet deposition and –48.9 μeq L^{-1} for throughfall. Less dominant, annual flux for throughfall deposition of Cl^- averaged 572 eq ha^{-1} yr^{-1} and NH_4^+ averaged 284 eq ha^{-1} yr^{-1} (Table 3-2). Throughfall deposition of base cations ranged from 284 eq ha^{-1} yr^{-1} to 790 eq ha^{-1} yr^{-1}. In general, annual wet deposition of ions was below 36% of throughfall, except for NH_4^+ at 78%. Mean annual NH_4^+ concentrations for wet deposition and throughfall were similar at 11.5 μeq L^{-1} and 13.3 μeq L^{-1}, respectively.

Calcium, NO_3^-, and SO_4^{2-} exhibited the greatest flux losses by stream export averaging 867, 771, and 671 eq ha^{-1} yr^{-1}, respectively (Table 3-2). Likewise, annual volume-weighted mean concentrations for these three ions were greater than others measured in the SW and NE streams (Table 3-3). Concentrations in the SW stream were: 48.4 μeq L^{-1} Ca^{2+}, 41.2 μeq L^{-1} NO_3^-, and

Table 3-3. Annual volume-weighted mean concentrations from 1991 to 2006 for hydrologic system compartments (WD = wet deposition; TF = throughfall; and A, Bw, and Cb = soil horizons). Based on ANOVA Tukey's HSD multiple comparison technique, data per parameter sharing same letters were not significantly different ($p \leq 0.05$).

Hydrologic System Compartments	Anion and cation concentrations (μeq L^{-1}); pH in standard pH units										
	Cl^-	SO_4^{2-}	$NO_3^- + NH_4^+$	NO_3^-	NH_4^+	pH	ANC *	Ca^{2+}	Mg^{2+}	K^+	Na^+
WD	10.2 ^{C}	25.6 ^{D}	22.3 ^{D}	10.8 ^{D}	11.5 ^{A}	4.7 ^{C}	-7.2	8.7 ^{E}	2.0 ^{D}	9.6 ^{B}	7.2 ^{C}
TF	26.4 ^{A}	81.8 ^{B}	52.0 ^{C}	38.8 ^{CD}	13.3 ^{A}	4.3 ^{E}	-48.9	40.8 ^{BC}	15.0 ^{C}	30.7 ^{A}	17.5 ^{B}
Soil A	27.3 ^{A}	93.7 ^{B}	129.2 ^{A}	126.9 ^{A}	2.3 ^{B}	4.0 ^{F}	-174.5	44.0 ^{BC}	24.9 ^{A}	27.6 ^{A}	24.4 ^{AB}
Soil Bw	25.7 ^{A}	91.9 ^{AB}	92.9 ^{B}	91.9 ^{B}	1.0 ^{B}	4.3 ^{DE}	-18.6	27.8 ^{D}	22.9 ^{AB}	12.8 ^{B}	23.8^{AB}
Soil Cb	26.1 ^{A}	83.7 ^{AB}	94.4 ^{B}	93.7 ^{B}	0.7 ^{B}	4.5 ^{D}	-30.0	37.1 ^{C}	25.1 ^{A}	11.8 ^{B}	19.3 ^{AB}
SW Stream	15.3 ^{BC}	29.4 ^{D}	41.7 ^{CD}	41.2 ^{C}	0.5 ^{B}	5.8 ^{A}	9.9	48.4 ^{AB}	18.8 ^{BC}	8.8 ^{B}	24.7 ^{A}
NE Stream	18.0 ^{B}	43.8 ^{C}	46.7 ^{CD}	46.0 ^{C}	0.7 ^{B}	5.5 ^{B}	2.4	53.3 ^{B}	21.2 ^{AB}	11.7 ^{B}	24.1 ^{AB}

* Stream ANC were measured for the 16-year period, but deposition and soil water ANC were only measured for years 2005 and 2006.

29.4 μeq L^{-1} SO_4^{2-}, and in the NE stream were: 53.3 μeq L^{-1} Ca^{2+}, 46.0 μeq L^{-1} NO_3^-, and 43.8 μeq L^{-1} SO_4^{2-}. Mean annual SO_4^{2-} and NO_3^- concentrations and net fluxes were lower in the SW stream than the NE stream. These results provide some explanation to the higher pH and ANC found in the SW stream than in the NE stream. Mean pH averaged 5.8 and 5.5, and ANC averaged 9.9 μeq L^{-1} and 2.4 μeq L^{-1} for the SW and NE streams, respectively. Mean annual NH_4^+ concentrations were 0.5 μeq L^{-1} and 0.7 μeq L^{-1} for the SW and NE streams, respectively, and mean net output of 11 eq ha^{-1} yr^{-1} was small compared to other ions (Table 3-2). Measured stream ions also included: Na^+, Mg^{2+}, Cl^-, and K^+ with net flux outputs averaging 443, 330, 306 and 182 eq ha^{-1} yr^{-1}, respectively.

Over this 16-year period in NDW, acid anions exhibited net retention in contrast to base cations that mostly showed net export, except for K^+ (Fig. 3-2). Net retention of SO_4^{2-} was greatest among the anions estimated at 61%, whereas Cl^- was estimated at 47% and NO_3^- at 11% (Table 3-2). Although NO_3^- retention appeared small, total inorganic nitrogen consisting of both NH_4^+ and NO_3^- was retained at 32%, presumably due to vegetative uptake. Evidence suggests most of NH_4^+ deposition is converted to NO_3^- in the upper soil layer because mean annual NH_4^+ concentration decreased, and NO_3^- and H^+ concentrations increased when water passed from throughfall to soil horizon A (Table 3-3). In addition, net NH_4^+ retention was estimated at 96%, assumed due to nitrification in the soil rather than adsorption. Consistent with the flux estimates for acid anions, annual volume-weighted mean concentrations of SO_4^{2-} and Cl^- were greater in the throughfall than the stream water. Net export of base cations from the streams, or depletion for Mg^{2+}, Ca^{2+}, and Na^+ were 16%, 10% , and 18%, respectively. Only one base cation exhibited net retention, which was K^+ at 71%.

Relationships Among Deposition, Soil, and Stream Water Chemistries

Between the hydrologic system compartments throughfall and soil horizon A, annual volume-weighted mean concentrations for several ions (Cl^-, SO_4^{2-}, Ca^{2+}, and K^+) were similar, within 10% of each other (Table 3-3). For example, SO_4^{2-} concentrations were 81.8 μeq L^{-1} and 93.7 μeq L^{-1}, and Ca^{2+} concentrations were 40.8 and 44.0 μeq L^{-1} for throughfall and soil horizon A, respectively. NH_4^+ was the only ion to be significantly greater in throughfall (13.3 μeq L^{-1}) compared to soil horizon A (2.3 μeq L^{-1}). In contrast, annual volume-weighted NO_3^- concentrations were significantly greater in soil horizon A compared to throughfall, with means differing by 88.1 μeq L^{-1}. Nitrification was inferred by these changes in NH_4^+ and NO_3^- concentration. Annual volume-weighted mean pH for throughfall and soil horizon A was 4.3 and 4.0, respectively, dropping 0.3 pH units between compartments. Annual volume-weighted ANC concentration means also dropped between these compartments from –48.9 μeq L^{-1} in throughfall to –174.5 μeq L^{-1} in soil horizon A.

Among all soil horizons (A, Bw, and Cb), mean annual volume-weighted concentrations of several ions were not statistically different; they were: Cl^-, SO_4^{2-}, NH_4^+, Mg^{2+}, and Na^+ (Table 3-3). Although statistically similar, NH_4^+ concentration in the A horizon (2.3 μeq L^{-1}) was less by 57% in B horizon (1.0 μeq L^{-1}). Mean annual volume-weighed NO_3^- concentrations in the A horizon (126.9 μeq L^{-1}) was significantly greater than in the Bw and Cb horizons (91.9 and 93.7 μeq L^{-1}, respectively). Mean annual cation concentrations for Ca^{2+} and K^+ were also found significantly greater in the A horizon from the Bw and Cb horizons. Except for Ca^{2+}, all ion were not statistically different between the Bw and Cb horizons. Calcium concentrations for the A, Bw, and Cb soil horizons were 44.0, 27.8, and 37.1 μeq L^{-1}, respectively. Mean annual pH of soil water of 4.0 in the A horizon was significantly less than in the Bw and Cb horizons (4.3 and 4.5,

respectively). Mean annual ANC also increased through the soil horizons from –174.5 μeq L^{-1} in the A horizon to –18.6 μeq L^{-1} in Bw horizon, and to –30.0 μeq L^{-1} in the Cb horizon.

Between soil horizon Cb and the NE and SW streams, mean annual volume-weighted concentrations were statistically different, except for NH_4^+, K^+, Mg^{2+}, and Na^+ (Table 3-3). Anion concentrations (SO_4^{2-}, NO_3^-, Cl^-) were significantly less in the stream than soil water. Sulfate concentrations were 29.4 and 43.8 μeq L^{-1} in the SW and NE streams, respectively; which were 65% and 48% lower than soil horizon Cb water of 83.7 μeq L^{-1}. Also, NO_3^- concentrations in the SW and NE streams of 41.2 and 46.0 μeq L^{-1}, respectively, approximately half that found in the horizon Cb. In contrast, Ca^{2+} concentrations were significantly more in the stream than soil horizon Cb, in which Ca^{2+} were 48.4 and 53.3 μeq L^{-1} in the SW and NE streams, respectively, and horizon Cb water was 37.1 μeq L^{-1}. In the SW and NE streams, pHs were 5.8 and 5.5, and ANC were 9.9 and 2.4 μeq L^{-1}, respectively; which were significantly greater than found in soil horizon Cb.

Precipitation event volumes measured as wet deposition and throughfall were significantly correlated with event concentrations for stream pH, ANC, SO_4^{2-}, and NO_3^-, indicating precipitation as a major factor in stream acidification response from acidic deposition ($p \leq 0.05$; Table 3-4). Stream pH, ANC, and NO_3^- biweekly event concentrations trended downward with increasing precipitation volumes, compared to stream SO_4^{2-} that trended upward (Fig. 3-3). Stream SO_4^{2-} and NO_3^- event concentrations were significantly correlated throughfall SO_4^{2-}, NO_3^-, and N event concentrations. Likewise, stream pH event measurements correlated directly with wet deposition and throughfall SO_4^{2-}, NO_3^-, NH_4^+, and N event concentrations. Stream ANC event concentrations positively correlated with wet deposition SO_4^{2-}, NO_3^-, and N event concentration, and throughfall SO_4^{2-}, but not throughfall NO_3^- and N.

Table 3-4. Statistical correlations between SW stream water event concentrations (pH, ANC, NO_3^-, and SO_4^{2-}), and wet and throughfall deposition water volumes and event concentrations (SO_4^{2-}, NO_3^-, NH_4^+, and N = NO_3^-& NH_4^+). Kendall τ-b values are only reported for significant correlations ($p \leq 0.05$); *ns* = non-significant.

		SW stream			
	Variable	pH	ANC	NO_3^-	SO_4^{2-}
Wet Deposition	Precipitation	-0.25	-0.21	-0.11	0.27
	SO_4^{2-}	0.23	0.20	-0.06	-0.14
	NO_3^-	0.18	0.14	*ns*	-0.16
	NH_4^+	0.12	*ns*	-0.12	-0.09
	N	0.16	0.09	-0.10	-0.13
Throughfall	Precipitation	-0.27	-0.26	-0.09	0.31
	SO_4^{2-}	0.18	0.21	*ns*	-0.13
	NO_3^-	0.10	*ns*	0.08	-0.13
	NH_4^+	*ns*	*ns*	*ns*	-0.13
	N	0.08	*ns*	0.07	-0.16

DISCUSSION

Stream acidification in NDW was co-dependent on acidic deposition, hydrology, and biogeochemical processes, including: annual mean flux inputs of SO_4^{2-} and NO_3^-; annual precipitation volumes; soil adsorption of SO_4^{2-}, nitrification rates in the soil A horizon related to annual precipitation; annual mean net export of base cations Ca^{2+}, Mg^{2+}, and Na^+ from soil sources; and K^+ retention likely from forest uptake. Deposition net fluxes of SO_4^{2-} and NO_3^- in the NDW were among the greatest ions, and SO_4^{2-} was about twice that of NO_3^-. In general, dominance of net SO_4^{2-} and NO_3^- fluxes in NDW deposition was consistent with other data across eastern United Stated (US) where streams have been impacted by acidic deposition (Driscoll et al., 2001; Sullivan et al., 2004; NADP, 2006).

In NDW, throughfall deposition of net SO_4^{2-} flux was about twice that found in lower elevation Mid-Atlantic watersheds, and around 300 eq ha^{-1} yr^{-1} lower than the empirical model predicted data of net sulfate deposition for this area (Dow and DeWalle, 1997; Castro and

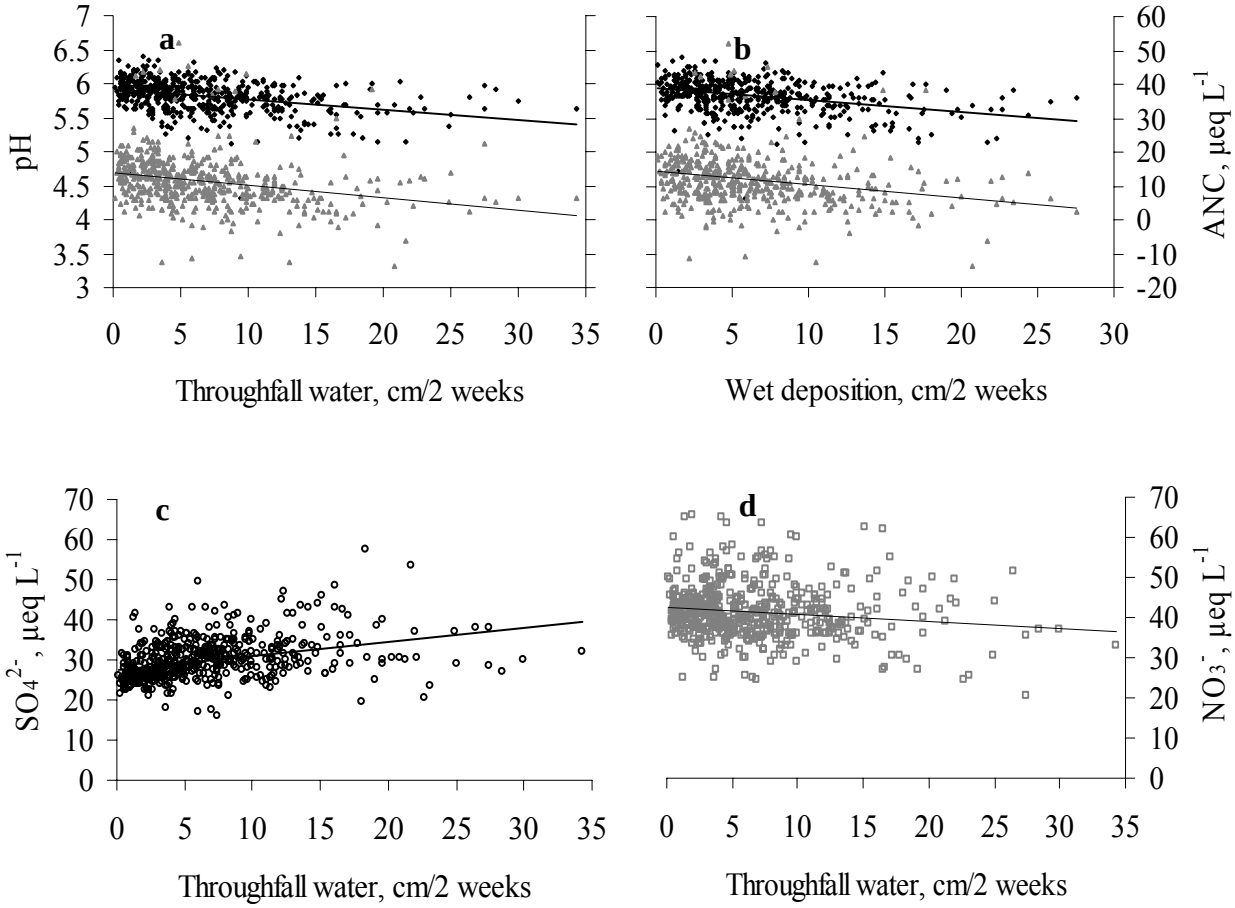

Fig. 3-3. Relationships between (a) SW stream pH (♦, $r^2 = 0.13$) and ANC (▲, $r^2 = 0.13$) vs. throughfall volume ; (b) SW stream pH (♦, $r^2 = 0.12$) and ANC (▲, $r^2 = 0.11$) vs. precipitation volume ; (c) SW stream SO_4^{2-} concentration (○, $r^2 = 0.13$) vs. throughfall volume; (d) SW stream NO_3^- concentration (□, $r^2 = 0.02$) vs. precipitation volume. Total observation numbers were 498 data points for throughfall samples, and 467 data points for wet deposition samples. Significance level for all data trends were $p \leq 0.01$.

Morgan, 2000; Weathers et al., 2006). Dry and cloud deposition of SO_4^{2-} throughfall fluxes can be roughly estimated by the difference of throughfall and wet deposition fluxes because canopy uptake rate of SO_4^{2-} is quite small in comparison (Cape et al., 1992; Johnson and Lindberg, 1992; Draaijers et al., 1997). It was approximately 70% of mean annual throughfall SO_4^{2-} total of 1,735 eq ha^{-1} yr^{-1}. Net sulfur input deposited by dry deposition at Look Rock, Tennessee (a CASTNet, low-elevation site in GRSM) ranged from 22% to 34% based on data between 1999 and 2007. The difference between NDW and Look Rock is likely due to elevation, where higher elevation watersheds receive more dry deposition than lower elevation watersheds (Weathers et al., 2006). It is also possible NDW receives additional sulfate inputs from cloud deposition. In the IFS study, net flux of sulfate deposition by cloud deposition was found to be approximately 48% in the NDW (Johnson and Lindberg, 1992).

Net N flux of throughfall deposition for NDW was found to be only half that predicted by the Weathers et al. (2006) regional model for acid deposition. In support of this finding, Draaijers and Erisman (1995) found net NO_3^- flux from measured dry deposition was approximately twice that computed by the difference between throughfall and wet deposition measurements. They attributed this difference to canopy uptake dynamics. Canopy uptake of NO_3^- and NH_4^+ as reported in literature suggests total inorganic N deposition will be underestimated (Johnson and Lindberg, 1992; Jin et al., 2006; Pajuste et al., 2006). In the IFS data, net dry throughfall deposition of NO_3^- was estimated at 752 eq ha^{-1} yr^{-1} compared with the total throughfall net of 1,241 eq ha^{-1} yr^{-1}, while about 50% of NH_4^+ input was added by cloud deposition (Johnson and Lindberg 1992). In addition, the IFS project found that uptake by the forest canopy of NO_3^- was 372 eq ha^{-1} yr^{-1} and NH_4^+ was 476 eq ha^{-1} yr^{-1}. As a result in the NDW, net retention of inorganic

N was expected to be more than 32% as reported, and nitrogen would be retained in the forest biomass.

Precipitation was found to be a major driver influencing how deposition acid anions were retained or exported in NDW, and the observed stream acidification response. Biweekly precipitation and throughfall volumes were inversely correlated with event stream pH and ANC. In addition, they were directly correlated with event SO_4^{2-} concentrations. Wet precipitation and throughfall SO_4^{2-} event concentrations were found to be directly correlated with stream event pH and ANC, and inversely correlated with stream SO_4^{2-} event concentrations. These results inferred that event deposition SO_4^{2-} was diluted by greater biweekly precipitation volumes because data analysis also found that biweekly throughfall SO_4^{2-} flux was inversely correlated with stream event pH and ANC, and directly correlated with stream SO_4^{2-} event concentrations ($r = -0.12$, -0.08, and 0.23, respectively). This illustrated precipitation events with greater biweekly volumes tended to rapidly transport SO_4^{2-} to the stream. High variability of the observed significant relationships may be attributed to different lengths of time between precipitation events, groundwater flow paths, and adsorption/desorption rates (Mulholland, 1993; Deyton et al., 2009). Soil adsorption and desorption of SO_4^{2-} are major factors to stream acidification (Driscoll et al., 1998; Evans et al., 1997; Mitchell et al., 2001). The role of soil adsorption/desorption processes on net export or retention dependents on watershed characteristics and acidic deposition history (Evans et al., 1997; Palmer et al., 2004; King et al., 2006). Overall in the NDW, net SO_4^{2-} retention of 61% was observed indicating long-term control by soil sorption. However, correlations among biweekly event data for precipitation, SO_4^{2-} concentrations, and stream pH and ANC suggest soil sorption SO_4^{2-} kinetics may also play an important role in the observed stream acidification responses.

In the NDW, net export of NO_3^- (771 eq ha^{-1} yr^{-1}) was observed similar to net SO_4^{2-} export (671 eq ha^{-1} yr^{-1}), suggesting biogeochemical processes related to N were equally important as SO_4^{2-} adsorption in regulating stream acidification response. Nitrification and forest uptake appear to be the dominant processes. Nitrification was implied by the significant increase of mean annual volume-weighted NO_3^- concentration and decrease of NH_4^+ concentration from throughfall to soil horizon A. The input-output budget found about 96% of net NH_4^+ input was converted to NO_3^-, and this percentage is not uncommon in forested watersheds (Johnson et al., 1991; Peterjohn et al., 1996; Willard et al., 1997). Nitrification appears to contribute to the observed mean annual pH of 4.0 in the upper soil horizon water, which was significantly lower than the mean annual pHs measured in throughfall and deeper soil horizons. Williard et al. (1997) suggests that soil nitrogen pools and dynamics related to microbial N cycling largely control watershed NO_3^- export. However, it appears that forest uptake also plays a key role in regulating net NO_3^- export to the stream. In the NDW, Johnson and Lindberg (1992) found that forest uptake was approximately 15% of net NO_3^- inputs, whereas our study found it to be about 32% of net total N input. Supporting the forest uptake assumption to account for net N retention, Barker et al. (2002) found that the annual N sequestering in aboveground biomass was 8 kg ha^{-1} yr^{-1} in a NDW study. Because nitrification and forest vegetation uptake are seasonally dependent on precipitation, and soil moisture and temperature, annual stream export of NO_3^- will vary based on yearly seasonal differences (Wright et al., 2001; van Miegroet et al., 2007). The influence of precipitation on N biological dynamics was observed by the generally weaker correlations among biweekly precipitation volumes, throughfall NO_3^- concentrations, and stream pH, ANC and NO_3^- concentrations.

Stream acidification in NDW appears to also be influenced by net base cation export. Base cations exported over the long-term included Ca^{2+}, Mg^{2+}, and Na^{+}, but not K^{+} which was observed to be retained at about 71%. Net K^{+} retention was assumed to be assimilated annually into forest biomass. Castro and Morgan (2000) also found K^{+} retention in a Maryland watershed, however net K^{+} export appears more typical among ion input-output budgets in northeastern U.S. (Watmough et al., 2005). Cation export from GRSM watersheds is of concern since it may impact the long-term health of forests (Tomlinson, 2003; Holzmueller et al., 2007). It appears prolonged acidic deposition has resulted in the loss of watershed base cations, where annual export fluxes are greater than weathering input fluxes (Fernandez et al., 2003; Lawrence, 2002; Tomlinson, 2003). In HBEF, net depletion of base cations appears to have increased watershed sensitivity to stream acidification and possibly has delayed recovery even as acidic deposition has declined (Driscoll et al., 2001). Others have also observed the importance of base cation availability in soils from weathering processes with regards to recovery of streams long impacted by acidic deposition (Sullivan et al., 2004; Houle et al., 2006).

Findings from this NDW study suggest that future conditions of stream water quality in high-elevation GRSM watersheds are dependent on several biogeochemical processes. Proton inputs from acidic deposition and nitrification proton generation in soils appear to lower soil water pH, and in term may regulate SO_4^{2-} adsorption. In some soil types, SO_4^{2-} sorption is increased by a decrease in soil water pH due to an increase positive charge on soil surface (Kölling and Prietzel, 1995; Gobran et al., 1998; Essington, 2004; Welsch et al., 2004). The influence of organic sulfur mineralization on net SO_4^{2-} export is less known (Spratt, 1998; Mitchell et al., 2001). In addition, the influence of mineralization of organic N and associated proton generation, and influence on stream acidification is not well understood in the NDW. Current export of base cations may be

moderating acidification of high-elevation streams in the GRSM, however if this cation pool becomes exhausted and acidic deposition persists, acidification of streams could accelerate in the future.

This long-term study provides essential information for use in a biogeochemical model in order to predict future conditions and depositional critical loads (Chen et al., 2004; Sullivan et al., 2004, 2007, 2008). Porter et al. (2005) cites the need for regional critical loads to protect aquatic resource protection of federal lands, including the GRSM. In the development of critical loads modeling, findings from this study illustrate the importance of understanding how annual precipitation volumes influence different biogeochemical processes, thus stream acidification response. This also emphasizes the need to incorporate the potential influence climate variability to depositional model scenarios (Deviney et al., 2006; Aherne et al., 2006; Wright et al., 2006). Continued long-term NDW monitoring through wet/dry cycles will provide valuable information on how climate patterns influence biogeochemical processes and stream water quality.

CHAPTER 4 LONG-TERM ANNUAL AND SEASONAL PATTERNS OF ACIDIC DEPOSITION AND STREAM WATER QUALITY IN A HIGH-ELEVATION GREAT SMOKY MOUNTAINS NATIONAL PARK WATERSHED

ABSTRACT

Evaluation of long-term and seasonal pattern of water chemistry in the Noland Divide Watershed (NDW), a high-elevation acidified watershed in the Great Smoky Mountains National Park (GRSM), provided insights into time trend and seasonal differences in deposition and water chemistry. An understanding of these differences will allow for a determination of how things change with decreases in deposition in the future. Long-term biweekly monitoring deposition and stream water quality data from 1991 to 2007 in NDW were used for statistical analysis of temporal trend and seasonal variation. The deposition fluxes and concentrations of sulfate and H^+ did not show significant trend over the time, despite the emission reduction of SO_2. Sulfate concentrations in streams remained stable and more than 50% retention of sulfate through this 17-year study period. For N compounds, increasing rates of nitrate and total inorganic nitrogen deposition concentrations were balanced by simultaneously decreasing rates of precipitation, resulting in insignificant change of deposition nitrogen flux. The retention amount of nitrogen was increased at the rate of 44.30 eq ha^{-1} yr^{-1}, likely caused by forest recovery from the intrusion of balsam woolly adelgid (*Adelges piceae*). The insignificant change of deposition and increasing trend of retention for nitrogen led the stream export of nitrate to significantly decline in both flux and concentration. Stream nitrate concentrate also showed a significant seasonal pattern, with concentrations being highest in leaf off season and lowest in summer, due to peak plant uptake of nitrogen in the growing season. Despite the declining nitrate concentration, stream acidification recovery, reflected by increasing ANC and pH, was not observed in the NDW. This insignificant change of stream acidity may be attributed to the declining export of base cations. Regression models with selected independent variables of deposition chemistry,

stream discharge, seasonal and temporal variations were constructed to predict the changes of stream pH, ANC, sulfate and nitrate concentrations. The analysis results of temporal trend and seasonal variations for deposition and stream chemistry in the NDW gave the resource managers a forecast of chemistry change in future and aided them better understanding the seasonal differences of chemistry around a year.

Key Words: acidic deposition; stream acidification, temporal trends; seasonal variation; water quality, Great Smoky Mountains

INTRODUCTION

Studies that concurrently investigate long-term trends in acidic deposition and stream water quality are crucial to understanding biogeochemical processes governing fate and transport of acid pollutants in watersheds, and the potential for recovery of stream water quality in acid sensitive regions (Driscoll et al., 1998; Jeffries et al., 2003; Vrba et al., 2003; Burns et al., 2006; Davies et al., 2007). Stream recovery from acidification would be expected due to emission reduction measures implemented at coal-fired power plants since the 1980's and observed reductions in sulfate deposition (Shannon, 1999; Driscoll et al., 2001; Stoddard et al., 2003). Reductions Lehmann et al. (2007) found in the eastern United States that sulfate deposition concentration decreased 46% from 1985 to 2004 in 141 out of 159 monitoring sites in sulfate deposition have been observed in North America and Europe (Forsius et al., 2003; Cooper and Jenkins, 2003; Driscoll et al., 2003; Jeffries et al., 2003). Although sulfate deposition has declined over the past two decades, stream acidification remains prevalent, underscoring the

long-term influence of biogeochemical processes governing recovery (Driscoll et al., 1995; Norton et al., 2004; Palmer et al., 2004; Davies et al., 2007).

Current research has attributed the lack of stream acidification recovery to: 1) desorption of sulfate from soils after several decades of deposition and soil adsorption; 2) deposition of nitrogen remaining constant; 3) depletion of base cation supply for streams; and 4) increased dissolved organic carbon entering streams (Likens et al., 1996; Gbondo-Tugbawa and Driscoll, 2002; Driscoll et al., 2003b; Jeffries et al., 2003; McCartney et al., 2003; De Wit et al., 2007). Most studies have shown a decrease of stream sulfate concentrations in response to reductions in sulfate deposition (Clow and Mast, 1999; Eimers et al., 2004; Webb et al., 2004; Burns et al., 2006). For example, Stoddard et al. (1999) reported in the northeastern United States that stream sulfate concentration in 25 watersheds decreased by 1.2 $\mu eq\ L^{-1}\ yr^{-1}$ in 1980's, and 0.9 $\mu eq\ L^{-1}\ yr^{-1}$ in 1990's. However, some watersheds export sulfate on a net annual basis (Castro and Morgan, 2000; Watmough et al., 2005). Recent efforts utilizing biogeochemical models suggest watershed recovery from acidic deposition may take several decades, governed mostly by base cations supply and nitrogen cycling dynamics (Chen et al., 2004; Sullivan et al., 2004, 2008; Aherne et al., 2006; Wright et al., 2006).

Nitrogen cycling, a function of plant uptake and microbial activities govern net annual nitrogen retention or export within a watershed (Dow and DeWalle, 1997; Williard et al., 1997; Chapman et al., 2001; Judd et al., 2007). These biological processes are influenced by climate and seasonal changes differing regionally, and augment variability of observed acidification responses and nitrogen export (Van Miegroet et al., 2001; Driscoll et al., 2003; Davies et al., 2007; Helliwell et al., 2007). Differences have been observed among studies. For example, net nitrogen export, primarily as nitrate has increased in Adirondack/Catskill mountains (Stoddard et

al., 1999), decreased in the Hubbard Brook Experimental Forest (Goodale et al., 2003), and remained relatively constant over time in other European streams (Forsius et al., 2003; Davies et al., 2007). Seasonally, nitrate leaching appears to be enhanced during cold winters in northern latitudes when soils freeze reducing nitrogen mineralization and plant uptake (Davies et al., 2007). In the Great Smoky Mountains National Park (GRSM) of southern Appalachia, Deyton et al. (2009) found episodic stream acidification governed by elevated stream nitrate concentrations during spring high flows prior to leaf growth.

Because trends and seasonal patterns in stream acidification response differ regionally, it is important to document responses where long-term data exists. Various studies have been conducted in the GRSM, but a detailed trend analysis at Noland Divide watershed (NDW) a high-elevation monitoring site has not utilizing coupled acid deposition and stream water quality data. Deposition, soil, and stream water quality data has been collected at NDW since 1991. A National Atmospheric Deposition Program (NADP) site at Elkmont approximately 14 km north of NDW and lower elevation has been reported a decline in sulfate concentration and flux since 1980, but not total inorganic nitrogen (NADP 2009). Also, Robinson et al. (2008) investigated trends in stream baseflow chemistry among elevation ranges finding sulfate concentration and pH declines between 1993 and 2002 in the lower elevation sites (< 1,060 m), but not at the higher elevations. No trends were observed for nitrate and acid neutralizing capacity (ANC) throughout that dataset. The ion input-output budget on NDW data from 1991 to 2006 find average net annual sulfate retention of 61%, nitrate retention of 32%, and net export of most base cations except potassium. This study did not investigate temporal trends or seasonal patterns of net ion flux. Lacking in the GRSM is information on long-term trends in net ion flux transport, temporally related to acid deposition flux and stream ion concentrations.

Utilizing the long-term NDW data for acid deposition and stream water quality, objectives for this study were: 1) document temporal trends in precipitation, throughfall, and stream chemistry; 2) characterize seasonal patterns in these chemistries; and 3) statistically model relationships between stream pH, ANC, SO_4^{2-} and NO_3^- with deposition dependent variables (i.e., precipitation volumes and frequency, deposition anions per event concentration and flux), Julian day and season, streamflow, and stream conductivity. The period of study was from 1991 through 2007. This analysis provides a temporal perspective to the ion input-output budget findings reported in Chapter 3. This study addresses the key regional question whether acid deposition has declined over the long-term and what changes in stream water chemistry has occurred within this period. In addition, this study summarizes essential data for the development of predictive models incorporating biogeochemical processes as system drivers.

METHODS

Field Sample Collection and Chemical Analyses

The NDW was equipped in 1991 with monitoring stations to measure atmospheric deposition as wet deposition (WD) and throughfall (TF), and water from the two headwater streams, identified as the southwest (SW) and northeast (NE) streams (Fig. 2-1). Monitoring from these stations began July 1991 and continues to the present. WD samples were collected biweekly at an open site (without forest cover) using a rainfall collector with an automated precipitation-triggered cover. TF samples were collected at one site approximately 50 m east of the open site using two open 5-gal plastic buckets. Beginning in 2005 during the frost-free periods, TF samples were collected with ten collector buckets covered and mounted with 90-mm diameter funnels to minimize evaporation. SW and NE stream samples were collected by grab method

weekly from 1991 to 2000 and biweekly since 2001. Most samples were collected during baseflow stages, and no effort was made to collect baseflow samples only. Each stream was equipped with a 3.0-ft H flume with stilling well and floating-type stage recorder connected to a Campbell CR10 data logger. Water stage measurements were recorded every 15 minutes, and discharge was calculated from depth according to standard H-flume tables in USDA-ARS (1979). Soil lysimeters were also monitored in the NDW, but soil water chemistry data were not used in this study analysis.

Samples were analyzed for pH, ANC, conductivity, SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, and base cations (BC = Ca^{2+}, Mg^{2+}, Na^+, K^+) at the University of Tennessee Water Quality Laboratory. Within 24 hours of collection, a ManTech™ autotitrator was used to analyze samples for pH, conductivity, and acid neutralizing capacity (ANC). ANC was obtained by Gran titration, used for low ionic strength waters (Hillman et al., 1986). To note, ANC measurements for WD and TF samples began in 2005, whereas stream samples were measured throughout the 16-year study period. Samples for ion concentrations were filtered by 0.4-µm membrane, separated into two sub-sample bottles, and refrigerated at 4°C until analyzed. Ions SO_4^{2-}, NO_3^-, Cl^-, and NH_4^+ were analyzed by ion chromatography. BC were analyzed by atomic absorption spectrometry (1991-1993, 1998-2003), and inductively coupled plasma spectrometry (2003-2007). Ions Na^+ and K^+ were measured by ion chromatography from 1993 to 1998, but Ca^{2+} and Mg^{2+} were not measured. Laboratory analyses met quality criteria set forth in a detailed quality assurance/ quality control program.

Water Volume, Ion Concentrations and Flux Computations

Water volumes for WD and TF were computed per collection, weekly from 1991 to 2000 and biweekly since 2001, converting measurements to a depth in cm based on the total surface area

of the collection bucket/funnels. Volumes were summed by month and as annual totals based on Julian year. SW stream exports were computed by summing measured volumetric discharges (m^3 s^{-1}) per 15-minute intervals into monthly and annual volumes (m^3), dividing volume estimates by watershed area and converting units to obtain estimates in cm.

Volume-weighted ion concentrations for WD, TF, and SW stream were computed for proton (pH), ANC, sulfate and inorganic nitrogen constituents annually per Julian year and on a monthly basis over the study period. To eliminate stormflow transport effects, only collection data during baseflow were used to compute the annual volume-weighted concentrations in this study. Samples collected when the event stream flow was greater than 0.0096 m^3 s^{-1} were excluded in the analysis.

Ion fluxes were summarized for proton, sulfate, and inorganic nitrogen constituents. WD and TF ion fluxes were computed by multiplying measurements of ion equivalents by total collector water volume, and dividing by the ratio of total collector funnel area to SW watershed area. Stream ion flux was computed by multiplying measurements of ion equivalents by discharge volumes over the collection period and SW watershed area. Flux estimates in eq ha^{-1} per weekly/biweekly measurements were summed by month, and annual totals based on Julian year. Net ion fluxes as watershed retention/detention were estimated by the difference between total deposition TF flux and SW stream export flux, summarized also by month and Julian year. Only the SW stream data was used in this study because flow patterns and ion concentrations and between NE stream and the SW stream were significantly correlated as stated in Chapter 3.

Data Analysis

Long-term temporal trends in pH, sulfate, and inorganic nitrogen constituents as annual volume-weighted concentrations and annual fluxes were statistically examined for WD, TF, SW

stream, and net retention. Linear regression models were developed per concentration and flux constituents on Julian year using JMP (v. 6.0.2). Temporal trends per constituent were determined by model coefficient sign on Julian year, and slope significance was inferred with a p-value less than 0.05. Analysis utilizing annual volume-weighted concentrations and fluxes because of the incomplete measurement for that year.

Using multiple regression, predictive models were developed for seasonality utilizing $\cos\theta$ and $\sin\theta$, where θ was computed by using the fraction of the year times two pi radians (Helsel and Hirsch, 2002). Monthly volume-weighted concentrations and fluxes for pH, sulfate, and inorganic nitrogen constituents were used in the analysis for the period 1991 through 2007. Seasonal trends using the predictive regression models were plotted with monthly means and 95% confidence interval.

Stepwise regression was used to develop predictive models for stream pH, ANC, and sulfate and nitrate concentrations. Regression models were constructed using SPSS 15.0 (SPSS, 2006), in which independent variables included cumulative Julian day, seasonality variables, TF deposition concentration and flux for sulfate and inorganic nitrogen constituents, SW stream discharge, and number of antecedent dry days prior the sampling day. Dry days per sample collection were determined by summing the number of days preceding the sample day and measurable daily precipitation at the Look Rock weather station. The Look Rock weather station is a National Park Service air monitoring station located about 16 km northwest of the NDW (NPS, 2010). Seasonality variables included $\cos\theta$ and $\sin\theta$, as defined above. Selection of the independent variables correlated with the response variable was based on the probability of the partial F statistic less than or equal to 0.05. Multicollinearity among independent variables was inspected using the variance inflation factor (VIF). A VIF value over 10 was an indication of

severe multicollinearity. The independent variable with the highest VIF value would be deleted from the model to generate the best adjusted r^2. In addition, Cook's Distance and partial residual plots were computed for each model to identify outliers of X_i or Y values. If those outliers were found to be unreasonable, those observations were deleted from the models.

RESULTS

Long-Term Annual Trends

Water Budget. From 1992 to 2007, annual WD and TF precipitation volumes declined, from estimates above 250 cm yr^{-1} in the early 1990's to about 200 cm yr^{-1} in recent years, a decrease of approximately 20% (Fig. 4-1a). However the last three years of record, southeastern United States was in severe drought. Two additional drought periods occurred in 1993 and 2000-2001. Over the 16-year period, significant annual declines in WD and TF precipitation were 6.29 cm yr^{-1} and 5.35 cm yr^{-1}, respectively ($p = 0.02$; Table 4-1). Annual mean discharges for the SW stream during this period declined from about 100 cm $yr^{-1}$to 60 cm yr^{-1}; however this decline was not significant in the NDW watershed ($p = 0.18$).

pH. Annual volume-weighted pH for TF was consistently recorded between 4.2 to 4.3 for the 16-year period (Fig. 4-1b). WD pHs generally followed the same temporal trends as TF but were in the order of 0.4 – 0.5 pH units greater. No significant long-term trend was observed for annual volume-weighted pHs for WD and TF ($p = 0.95$, 0.51, respectively; Table 4-2). Annual proton flux trended downward over time for WD and TF, however the trend on an annual basis was not significant ($p = 0.42$, 0.21, respectively; Table 4-1). Likewise, annual volume-weighted pHs for the SW stream remained around 5.8 without a significant temporal trend ($p = 0.67$, Table 4-2; Fig. 4-1b). Annual proton flux in the SW stream trended upward over time slightly, but was

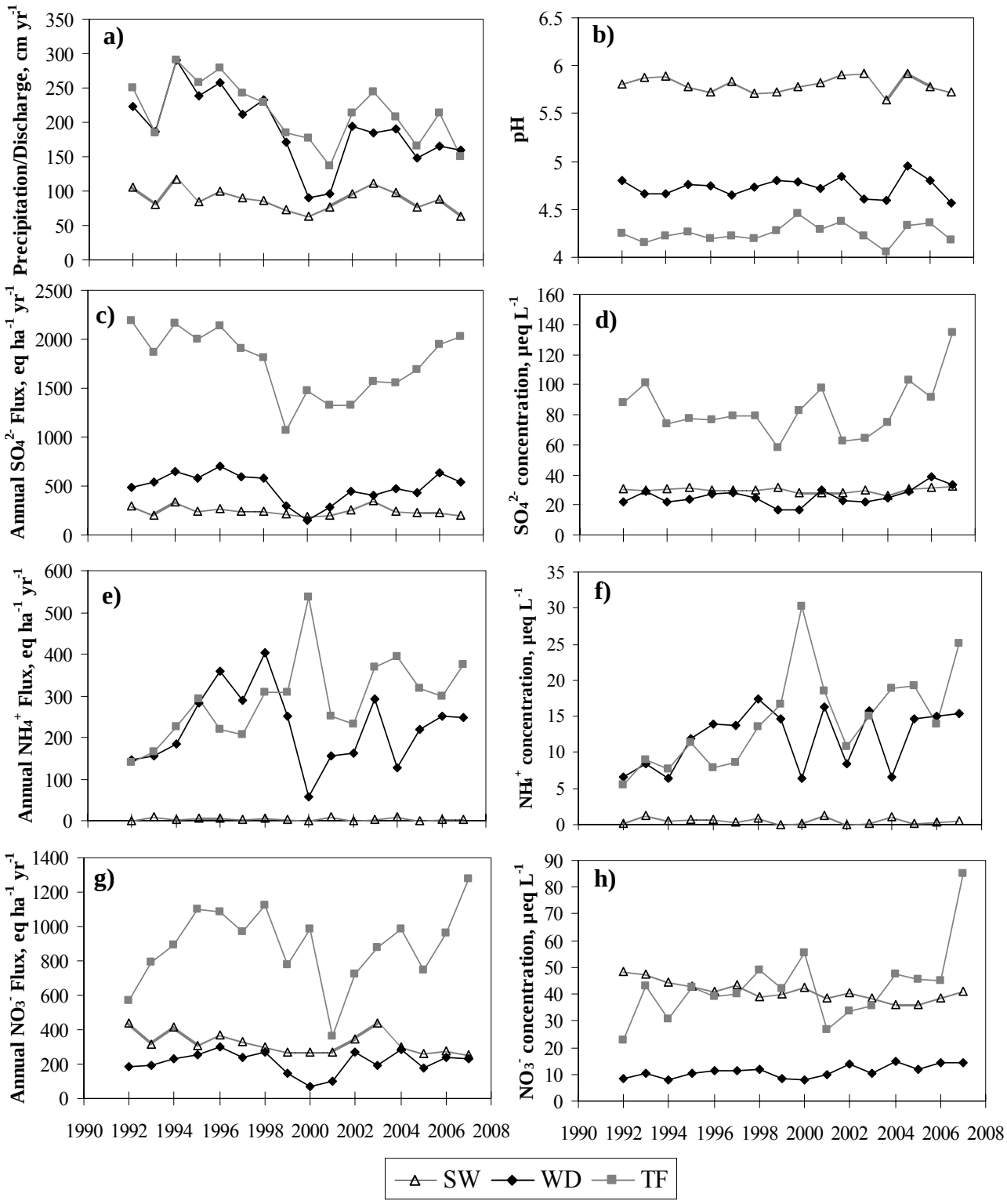

Fig. 4-1. Annual precipitation, stream discharge, pH, ANC, SO_4^{2-} and NO_3^-/NH_4^+ flux and annual volume-weighted concentration for deposition and stream outflow from 1992 to 2007 . WD = wet deposition, TF = throughfall, SW = southwest stream.

Table 4-1. Temporal trends for annual precipitation and stream discharge (cm yr^{-1}); and annual ion flux and net annual ion flux (eq ha^{-1} yr^{-1}) in the NDW from 1992 to 2007 (n =16) . Significant regression models are shown in bold ($p \leq 0.05$).

Sites	Parameters	Precipitation / Discharge	H^+	SO_4^{2-}	NO_3^-	NH_4^+	N[1]
WD	Slope per Julian year	**-6.29**	-8.05	-7.77	-0.26	-0.51	-0.77
	R^2	0.31	0.05	0.06	0.00	0.00	0.00
	p value	**0.02**	0.42	0.35	0.94	0.92	0.92
TF	Slope per Julian year	**-5.35**	-29.64	-26.97	7.98	**12.36**	20.35
	R^2	0.31	0.11	0.14	0.03	0.36	0.12
	p value	**0.02**	0.21	0.15	0.53	**0.01**	0.19
SW	Slope per Julian year	-1.18	0.35	-2.89	**-6.72**	-0.12	**-6.84**
	R^2	0.13	0.10	0.08	0.26	0.04	0.27
	p value	0.18	0.23	0.29	**0.04**	0.47	**0.04**
Ret.[2]	Slope per Julian year		-29.84	-10.89	**31.69**	**12.60**	**44.30**
	R^2		0.11	0.03	0.27	0.36	0.35
	p value		0.20	0.54	**0.04**	**0.01**	**0.02**

WD = wet deposition, TF = throughfall, SW = southwest stream, n = number of observations

[1] N represents the inorganic nitrogen by summing NO_3^- and NH_4^+
[2] Ret. represents net annual ion flux (TF – Total stream export)

Table 4-2. Temporal trends for annual volume-weighted concentrations (μeq L^{-1}) in the NDW from 1992 to 2007 (n = 16). Significant regression models are shown in bold ($p \leq 0.05$).

Sites	Parameters	pH	SO_4^{2-}	NO_3^-	NH_4^+	N[1]
WD	Slope per Julian year	0.00	0.47	**0.34**	0.35	**0.69**
	R^2	0.00	0.16	0.46	0.17	0.39
	p value	0.95	0.13	**< 0.01**	0.12	**0.01**
TF	Slope per Julian year	0.00	1.16	**1.56**	**0.94**	**2.51**
	R^2	0.03	0.09	0.28	0.44	0.39
	p value	0.51	0.27	**0.04**	**< 0.01**	**0.01**
SW	Slope per Julian year	0.00	-0.02	**-0.61**	-0.01	**-0.62**
	R^2	0.01	0.00	0.66	0.02	0.68
	p value	0.67	0.85	**< 0.01**	0.59	**< 0.01**

WD = wet deposition, TF = throughfall, SW = southwest stream, n = number of observations

[1] N represents the inorganic nitrogen by summing NO_3^- and NH_4^+

also not significant (p = 0.23; Table 4-1).

Sulfate. Annual volume-weighted SO_4^{2-} concentrations and flux for TF were greater and more variable than WD over the 16-year study period (Figs. 4-1c and 4-1d). TF SO_4^{2-} concentrations ranged from 58 to 135 μeq L^{-1} and flux ranged from 1,070 to 2,200 eq ha^{-1} yr^{-1}. WD SO_4^{2-} concentrations remained near 30 μeq L^{-1}, and flux remained mostly near 500 eq ha^{-1} yr^{-1} although the range was from 150 to 700 eq ha^{-1} yr^{-1}. Yearly TF variation of SO_4^{2-} concentrations was usually associated with precipitation amount with dry years tending to be greater in SO_4^{2-} concentration. In 2007, a regionally severe dry year, the annual volume-weighted throughfall SO_4^{2-} concentration was 135 μeq L^{-1}, the highest recorded estimate, and much greater than the overall average of 84 μeq L^{-1}. No significant long-term trends in annual volume-weighted SO_4^{2-} concentrations and flux were observed for WD and TF (Tables 4-1 and 4-2).

Compared to depositional measurements, annual volume-weighted SO_4^{2-} concentrations and

flux for the SW stream was less variable over time (Figs. 4-1c and 4-1d). SW stream SO_4^{2-} concentrations remained about 30 μeq L^{-1} and flux remained about 250 eq ha^{-1} yr^{-1}. Although the long-term trends in annual volume-weighted SO_4^{2-} concentrations and flux were downward, they were not significant (Tables 4-1 and 4-2). As observed by the annual flux differences in depositional measurements and stream export, NDW functioned as a SO_4^{2-} sink in which annual net retention ranged from 450 to 1,550 eq ha^{-1} yr^{-1} (Fig. 4-2). The average annual net SO_4^{2-} estimates for retention was 1,100 eq ha^{-1} yr^{-1} for the 16 years. No significant temporal trend in annual net SO_4^{2-} retention was observed ($p = 0.54$; Table 4-1).

Inorganic Nitrogen. Annual volume-weighted NH_4^+ concentrations and flux for TF significantly increased over the study period at a yearly rate of 0.94 μeq L^{-1} and 12.36 eq ha^{-1} yr^{-1}, respectively ($p < 0.01$, $p = 0.01$, Tables 4-1 and 4-2). NH_4^+ concentrations varied from 6 to 30 μeq L^{-1}, and flux ranged from 140 to 540 eq ha^{-1} yr^{-1} (Figs. 4-1e and 4-1f). TF concentrations and flux measurements that were well above the general trend line coincided with low annual precipitation volumes (Fig. 4-1). Annual volume-weighted NH_4^+ concentrations for WD did not

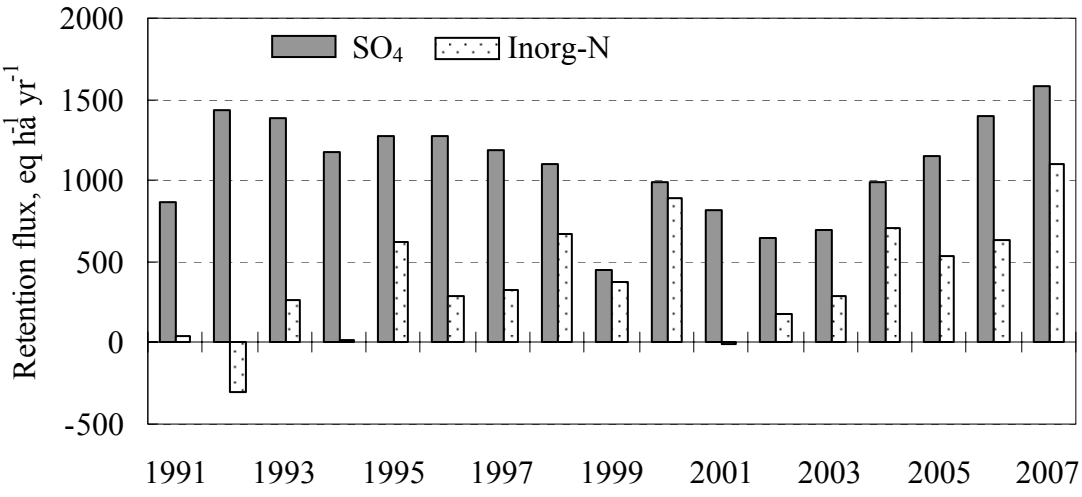

Fig. 4-2. Annual net retention/depletion in the NDW for sulfate and inorganic nitrogen flux.

exhibit significant trends (Tables 4-1 and 4-2).

Annual volume-weighted NO_3^- concentrations for TF significantly increased at an annual rate of 1.56 μeq L^{-1} yr^{-1} ($p = 0.04$; Table 4-2), however the measurement for 2007 greatly exceeded previous measurements by 30μeq L^{-1} (Fig. 4-1h). Annual NO_3^- flux did not exhibit a significant trend (Fig. 4-1g; Table 4-1). Annual volume-weighted NO_3^- concentrations for WD significantly increased at a yearly rate of 0.34 μeq L^{-1} ($p < 0.01$; Table 4-2); however WD NO_3^- flux was not significant (Table 4-1). Annual volume-weighted inorganic N concentrations, NH_4^+ and NO_3^- summed, significantly increased for both TF and WD over the study period at annual rates of 2.51 and 0.69 μeq L^{-1}, respectively ($p = 0.01$; Table 4-2). However, long-term trends for TF and WD inorganic N annual fluxes increased, but trend lines were not statistically significant.

In the SW stream, annual volume-weighted NH_4^+ concentrations were less than 1 μeq L^{-1}, in contrast to NO_3^- concentrations that ranged from 36 to 47 μeq L^{-1} (Figs. 4-1f and 4-1h). Similarly, annual NH_4^+ flux export from the SW stream was less than 1 eq ha^{-1} yr^{-1}, in contrast to NO_3^- that ranged from 252 to 440 eq ha^{-1} yr^{-1} (Figs. 4-1e and 4-1g). A net loss of NH_4^+ occurred after atmospheric deposition prior to stream transport, where nitrogen was mainly exported as NO_3^-, even though 25% of the total deposition of inorganic N was in the form of NH_4^+. In the SW stream, long-term trends for volume-weighted NO_3^- concentrations significantly declined at an annual rate of 0.61 μeq L^{-1} and flux at a rate of 6.72 eq ha^{-1} yr^{-1} ($p < 0.01$, 0.04, respectively; Tables 4-1 and 4-2). Annual net retention of inorganic N in the NDW significantly increased at the rate of 44.30 eq ha^{-1} yr^{-1} (Table 4-1). Overall, annual net inorganic N was retained in the NDW (Fig. 4-2). Although it was observed to be highly variable from net export of about 300 eq ha^{-1} yr^{-1} in 1992 to a maximum net retention of 1,100 eq ha^{-1} yr^{-1} in 2007.

Base Cations. Annual volume-weighted BC concentrations in the SW stream, as represented

by Ca^{2+}, Na^{+}, Mg^{2+}, and K^{+} were portioned by the following average percentages: 47.5%, 25.5%, 18.5%, and 8.5%, respectively (Fig. 4-3). For most years, the BC concentrations after 1998 were lower than the measurements in the early 1990s. Between 1999 and 2007, event BC concentrations declined at the rate of 0.0014 μeq L^{-1} day^{-1} ($p = 0.02$, $n = 251$), although the trend expressed by annual volume-weighted concentrations was insignificant. The decreasing BC trend was primarily attributed to reductions in event K^{+} concentrations. Trends in SW stream event concentrations for Ca^{2+} and Na^{+} were insignificant over time, whereas Mg^{2+} event concentrations showed a significant upward trend of 0.0006 μeq L^{-1} day^{-1} ($p < 0.01$).

Monthly Seasonal Patterns

Water Budget. Seasonally, WD and TF precipitation were lowest during summer (Fig. 4-4a). In July, TF volumes averaged about 12 cm $month^{-1}$, which were about half the peak winter TF volumes from November through March. TF volumes tended to be greater than WD volumes in most seasons except in summer July and August when evapotranspiration is highest and

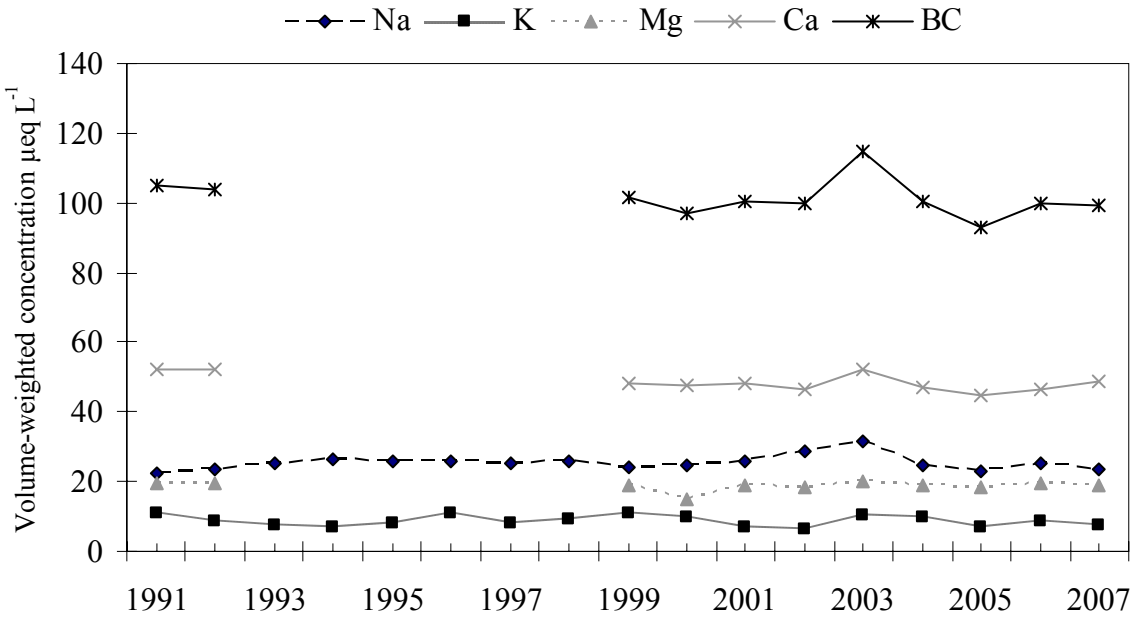

Fig. 4-3. Annual volume-weighted concentrations of base cations (BC) in SW stream from 1991 to 2007. Note, Mg^{2+} and Ca^{2+} measurement were not available from 1993 to 1998.

appeared to influence TF/WD relative portions. The SW stream monthly discharges were generally lower during the leaf-on periods May through October averaging about 5 cm $month^{-1}$ (0.0031 m^3 s^{-1}). The monthly mean discharge was lowest in September, which was about 1 to 2 month lag from the lowest mean monthly precipitation volumes. Monthly discharges in the SW stream were highest when leaves are off December through March averaging about 10 cm $month^{-1}$ (0.0062 m^3 s^{-1}).

pH. Mean monthly volume-weighted TF pH was lowest in the spring March through May ranging from 4.0 to 4.2, and highest in the fall during October and November at about 4.3 (Fig. 4-4b). Mean monthly WD pH was found lowest during summer periods June through August ranging from 4.5 to 4.6. In contrast, mean monthly volume-weighted pH in the SW stream were lowest from December through February at about 5.7. Mean monthly pH in the SW stream tended to be highest during summer and early fall (May through October) ranging between 5.8 and 5.9. In general, variability in monthly pH means in the SW stream was less than means observed with WD and TF.

Sulfate. Mean monthly SO_4^{2-} fluxes for TF averaged 155 eq ha^{-1} $month^{-1}$ and did not vary seasonally, although monthly WD flux was observed to be greater during the months of March through September (Fig. 4-4c). In general, WD monthly fluxes of SO_4^{2-} were 1/4 to 1/3 of TF. Mean monthly SO_4^{2-} concentrations for TF and WD were highest during summer at 160 μeq L^{-1} and lowest in winter at 80 μeq L^{-1} (Fig. 4-4d). Compared to depositional measurements, long-term SO_4^{2-} averages of monthly SW stream flux declined during summer and fall months from May through October, and ranged approximately from 25 to 40 eq ha^{-1} $month^{-1}$. Average monthly volume-weighted concentrations for SW stream SO_4^{2-} remained relatively constant throughout the year at about 25 μeq L^{-1}. As summer is the dry season in this region, stream

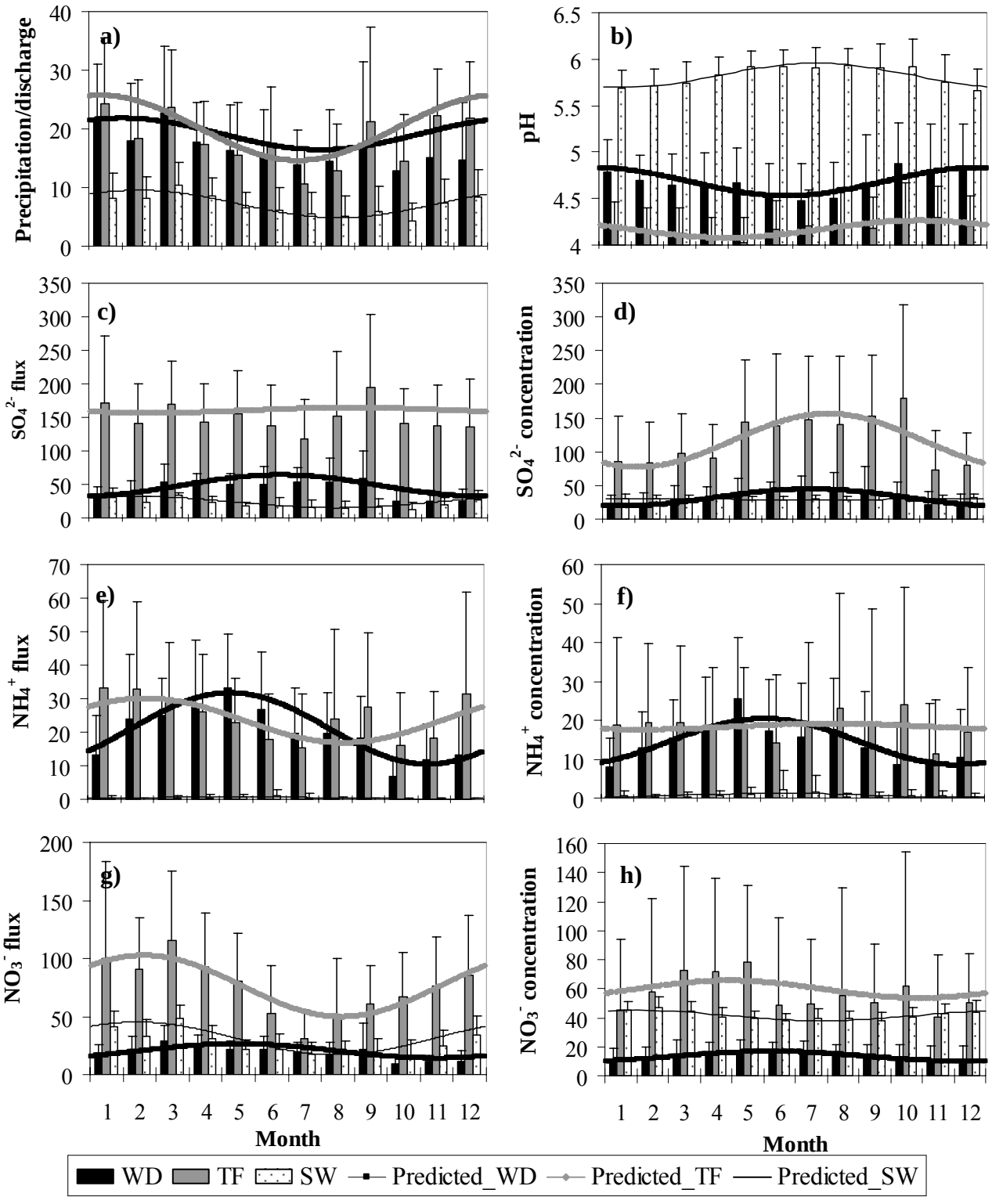

Fig. 4-4. Seasonal variation of precipitation/discharge (cm $month^{-1}$), pH, SO_4^{2-} and inorganic nitrogen flux (eq ha^{-1} $month^{-1}$) and concentrations (μeq L^{-1}) in wet and throughfall deposition (WD/TF) and SW stream export. Month 1 = January; 12 = December.

export of SO_4^{2-} average monthly flux was minimum, indicating SO_4^{2-} retention was maximum during summer.

Inorganic Nitrogen. Mean monthly NH_4^+ fluxes for TF and WD flux were seasonally variable, where TF peaked during winter months December through February, and WD peaked in May (Fig 4-4e). Mean monthly NH_4^+ flux for TF was lowest in July 16 eq ha^{-1} yr^{-1} and for WD it was during October at about 7 eq ha^{-1} yr^{-1}. Mean monthly NH_4^+ concentration for WD also peaked during May and was lowest in October; however mean monthly NH_4^+ concentrations for TF exhibited no seasonal patterns (Fig. 4-4f). In the SW stream, mean monthly NH_4^+ concentrations and flux exhibited no seasonal patterns, and were minimal compared to NO_3^- concentrations and flux (Figs. 4-4e –h).

Mean monthly NO_3^- flux for TF was seasonally variable, ranging from 30 to 115 eq ha^{-1} yr^{-1} (Fig. 4-4g). These values were greater during winter months and peaked in March. WD fluxes were slightly greater during summer months than winter ranging from 9 to 29 eq ha^{-1} yr^{-1}. Mean monthly NO_3^- concentrations for TF and WD were generally greater during spring and summer months and lower during winter months (Fig. 4-4h). TF peaked in May at about 78 eq ha^{-1} yr^{-1}.and WD peaked May through July at about 16 eq ha^{-1} yr^{-1}. In the SW stream, mean monthly NO_3^- concentrations and fluxes were generally greater during winter than summer with a seasonal range less pronounced compared to NO_3^- deposition measurements. Mean monthly NO_3^- concentrations in the SW stream ranged from 39 to 47 μeq L^{-1} and fluxes ranged from 17 to 50 eq ha^{-1} yr^{-1}.

Statistical Models for Stream pH, ANC, Sulfate and Nitrate Concentrations

Four significant regression models were developed per dependent variables: SW stream pH, ANC, SO_4^{2-} and NO_3^- concentrations ($p < 0.01$; Table 4-3). Seasonal variables ($\cos\theta$, $\sin\theta$) were

strongly selected as predictors by the stepwise procedure for pH, ANC and NO_3^-, but not SO_4^{2-}. These results were consistent with seasonal patterns observed in Fig. 4-4. Julian day was not selected in the regression models for stream pH, ANC and SO_4^{2-}, indicating these ion concentrations were not changing significantly with time. However, Julian day was selected in the stream NO_3^- model with a negative slope indicating this ion was declining over time. These results with Julian day were consistent with the temporal trend analyses (Tables 4-1 and 4-2).

Number of dry days antecedent the sampling day had a substantial influence on stream pH and SO_4^{2-} (Table 4-3). Stream pH was directly correlated with number of dry days. In contrast, stream SO_4^{2-} was negatively correlated with number of dry days. Stream pH was negatively correlated with WD event precipitation, but other models were not correlated with this variable. Stream pH, ANC, and NO_3^- event concentrations were negatively correlated with stream discharge, whereas stream SO_4^{2-} was directly correlated.

In general, the four regression models correlated with WD event concentrations and fluxes over TF, except for stream SO_4^{2-} (Table 4-3). Stream pH was directly correlated with WD event SO_4^{2-} concentration, and negatively correlated with WD event proton fluxes and TF N event concentrations. The stream pH model predicted an increasing rate of 0.003 pH units per year. Stream ANC was directly correlated with WD event SO_4^{2-} concentration. It was negatively correlated with WD event conductivity and proton flux, and TF event Cl^- flux. Stream NO_3^- was directly correlated with WD event SO_4^{2-} concentration, and negatively correlated with WD event N event concentrations and NH_4^+ flux. Uniquely, stream SO_4^{2-} was directly correlated with TF event SO_4^{2-} flux and negatively correlated with TF event SO_4^{2-} concentration.

Table 4-3. Predictive models for stream pH, ANC, SO_4^{2-} and NO_3^-. Ion concentrations were expressed in μeq L^{-1}; annual flux in eq ha^{-1} yr^{-1}; WD and TF precipitation in cm/sampling period; and stream discharge in m^3 s^{-1}.

$$SW\_pH = 5.8946 - 0.0893\cos(\theta) - 0.0328\sin(\theta) + 0.0203 dry\_days - 6.3074 SW\_Q - 0.0050 WD\_Prec + 0.0024 WD\_SO_4 - 0.0004 TF\_N - 0.0001 WD\_H\_Flux$$

n = 437; $r^2_{Adj} = 0.3427$; $p < 0.01$

$$SW\_ANC = 14.2405 - 3.3273\cos(\theta) - 2.1971\sin(\theta) - 172.2226 SW\_Q + 0.1277 WD\_SO_4 - 0.2300 WD\_Cond - 0.0018 WD\_H\_Flux - 0.0016 TF\_Cl\_Flux$$

n = 443; $r^2_{Adj} = 0.2763$; $p < 0.01$

$$SW\_SO_4 = 28.4911 - 0.3065 Dry\_day + 244.3675 SW\_Q - 0.0118 TF\_SO_4 + 0.0010 TF\_SO_4\_Flux$$

n = 482; $r^2_{Adj} = 0.2535$; $p < 0.01$

$$SW\_NO_3 = 107.1053 - 0.0018 Julian\_Day + 4.0516\cos(\theta) + 2.5462\sin(\theta) - 212.6996 SW\_Q + 0.0699 WD\_SO_4 - 0.0451 WD\_N - 0.0029 WD\_NH_4\_Flux$$

n = 457; $r^2_{Adj} = 0.3983$; $p < 0.01$

SW = southwest stream, WD = wet deposition, TF = throughfall, Q = stream discharge; θ = fraction of days in one year × 2π; Cond = conductivity; Prec = precipitation; and n = number of observations

DISCUSSION

Analysis of long-term trends for NDW deposition found a mean annual decline in precipitation water (6.29 cm yr^{-1} for WD and 5.35 cm yr^{-1} for TF), increases in TF NH_4^+ concentrations and fluxes (0.94 μeq L^{-1} yr^{-1} and 12.36 eq ha^{-1} yr^{-1}), and increases in WD and TF NO_3^- concentrations. No trends were observed for WD and TF mean annual pHs ranging from 4.6-4.8 and 4.2-4.3, respectively. In addition, no significant trends were observed for mean annual SO_4^{2-} deposition, although it appeared to have declined at –7.77 eq ha^{-1} yr^{-1} for WD and –26.97 eq ha^{-1} yr^{-1} for TF over the study period 1992 through 2007. However, annual volume-weighted SO_4^{2-} concentrations for WD and TF showed slight upward trends at 0.47 μeq L^{-1} yr^{-1} and 1.16 μeq L^{-1} yr^{-1}, respectively. This inverse result between SO_4^{2-} flux and concentration is apparently due to the significant decline in precipitation during this period. The non-significant SO_4^{2-} deposition trends could be due to the statistics utilizing annual means (df = 15).

Overall, other regions have reported a significant decline in sulfate deposition in terms of flux in northeastern US, Ontario Canada, and northern Europe (Stoddard et al., 1999; Eimers and Dillon, 2002; Folster et al., 2003; Forsius et al., 2003; Watmough et al., 2005). During the early 1990's, Stoddard et al. (1999) estimated annual SO_4^{2-} deposition declines of 0.9 μeq L^{-1} yr^{-1} over the Adirondick-Catskill region, and of 3.5 μeq L^{-1} yr^{-1} over New England-Quebec region. In this study regional differences were significant. It appears since the 1990's that declines in sulfate deposition has diminished. In the Adirondick-Catskill region, Burns et al. (2006) found significant declines in precipitation SO_4^{2-} concentrations from 1984 through 2001, but not from 1992 through 2001. Similarly, an analysis of the NADP (2009) data at the GRSM Elkmont site found a significant decline of precipitation SO_4^{2-} concentrations of 0.63 μeq L^{-1} $yr^{-1}$from 1984

through 2007, but not during the period 1992 through 2007. It appears the rate of SO_4^{2-} deposition declines may have waned in recent years, but the finding from NDW illustrates the potential influence of drier climatic patterns on SO_4^{2-} concentrations.

Consistent with the national findings in Lehmann et al. (2007), NH_4^+ deposition has increased 28.5% between 1985 and 2004 based on 159 NADP sites. Although, this study attributes the increase from agricultural sources, others have noted slight increased in N deposition from vehicular sources (Driscoll et al., 1995). NADP (2009) data at the GRSM Elkmont site for the period 1992 through 2007 showed a non-significant increase in precipitation NH_4^+ concentrations of 0.14 μeq L^{-1} yr^{-1}, which compares with the NDW increase of 0.35 μeq L^{-1} yr^{-1} for the same period. The dominant increase at NDW has been in the flux to the soil from TF, estimated at 12.36 eq ha^{-1} yr^{-1}. TF NO_3^- deposition flux has also increased, estimated at 7.98 eq ha^{-1} yr^{-1} and a significant NO_3^- concentration increase of 1.56 μeq L^{-1} yr^{-1}. Much like mean annual SO_4^{2-} concentrations in TF trends, NH_4^+ and NO_3^- concentrations were notably greater when precipitation volumes were less relative to the general trend line.

Precipitation is a dominant driver in the fate and transport of SO_4^{2-} to the stream. An inverse relationship between WD volumes and SO_4^{2-} concentrations in NDW suggests ion dilution occurs with increased precipitation on an annual basis. Seasonally, TF SO_4^{2-} concentrations were the greatest during summer apparently from reduced TF volumes and accumulating dry deposition. Precipitation patterns can influence SO_4^{2-} retention annually by influencing soil desorption-adsorption rates (Palmer et al., 2004; Burns et al., 2006; King et al., 2006). In general during this period, average net SO_4^{2-} flux has been retained about 61% (Chapter 3). Precipitation volumes and SO_4^{2-} deposition concentration govern soil adsorption where increased concentration promotes greater adsorption if precipitation rates over time allow for SO_4^{2-} to be

effectively transported into the soil horizons (discussed in Chapter 7). If precipitation rates are relatively high over time, interflow through the soil promotes transport to the stream rather than adsorption and retention.

Illustrating the results of the soil hydrologic and geochemical processes, stream SO_4^{2-} concentrations in NDW were directly correlated with stream discharge, TF SO_4^{2-} flux, and number of dry days. Stream SO_4^{2-} concentrations were indirectly correlated with TF SO_4^{2-} concentration, inverse to flux relations and assumed to be a function of SO_4^{2-} dilution during periods of elevated precipitation. Because no long-term trends in stream SO_4^{2-} concentrations were observed, and watershed SO_4^{2-} retention dominates annually, annual net flux output is strongly by the soil adsorption capacity under current SO_4^{2-} and proton flux inputs (Chapter 6). Eimers and Dillion (2002) found instream SO_4^{2-} concentrations correlated with number of dry days in a low-elevation Ontario stream, which was consistent with NDW. However, they found an inverse relation with stream SO_4^{2-} concentrations and discharge suggesting a dilution effect occurs instream differing from the NDW. Mountainous terrain and soil properties in the NDW where interflow hydrology dominates ion transport rather than runoff could explain differences in the stream SO_4^{2-} concentrations and discharge relationships. The influence of soil mineralization rates of organic S is also another possible process to concern (Driscoll et al., 1998; Gbondo-Tugbawa and Driscoll, 2002).

Precipitation is a dominant driver in the fate and transport of inorganic nitrogen to the stream also, primarily as NO_3^- in the stream. Like SO_4^{2-}, an inverse relationship between WD volumes and NH_4^+ concentrations in NDW suggests ion dilution occurs with increased precipitation on an annual basis. Most of the NH_4^+ in deposition is converted to NO_3^- in the soil, in which vegetation uptake retains approximately 32% of the net N flux entering NDW over the study period

(Chapter 3). The retention amount of nitrogen was increasing at the rate of 44.3 eq ha^{-1} yr^{-1}, primarily because of the increasing uptake by plant in this watershed. Due to the infestation of balsam woolly adelgid (BWA, *Adelges piceae*, Ratzeburg), a severe dieback of Frasier fir was observed during 1970's. Current information shows an increase in young trees which are taking up more nitrogen than was observed in 1990s (Jenkins, 2007; van Miegroet et al., 2007). The nitrogen uptake by overstory vegetation between 1993 to 1998 was measured to be 8 kg ha^{-1} yr^{-1} (Barker et al., 2002). Moore et al (2007) measured the uptake to be 11-15 kg ha^{-1} yr^{-1} between 1999 and 2004. It indicated that more nitrogen was assimilated by vegetation recently. As a result, the stream export of nitrate was decreasing from 1992 to 2007.

The influence of vegetation uptake on stream NO_3^- can be observed seasonally in which stream NO_3^- concentration and flux are greater during the winter months. Low biotic demand and snowmelt export of nitrogen in dormant season increased the amount of nitrogen export during winter. In contrast, high biotic activity and plant uptake in summer elevated the retention amount of nitrogen within the watershed so that to reduce the stream export in this season (Castro and Morgan II, 2000; Mitchell, 2001; Wright et al., 2001).

The seasonal pattern of nitrogen also influenced the seasonal variation of stream pH and ANC. The seasonal lowest nitrate concentration in summer increased stream pH and ANC to the highest values during this season. This is because plant uptake of nitrogen in growing season offset some acidity, leading to the reduction of export of proton and the increase of pH and ANC at that season. The seasonal pattern of hydrological cycle is the other possible causes to the seasonality of pH and ANC. Long residence time associated with dry season summer enhances the reaction of acidic water with soil cations to neutralize added hydrogen and raise stream pH. The relationship of hydrological cycle and stream water chemistry indicated that climate

variability would be one of important factors for stream recovery from acidification (Aherne et al., 2006; Wright et al., 2006).

Stream recovery from acidification was expected due to decreasing nitrate concentration and stable sulfate concentration. However, no statistically significant increase of ANC and pH were observed during this study period. It was found that the declining rate of total base cation concentration in stream was at the same level of the declining rate of nitrate concentration. As ANC is expressed by the difference of total base cations and anions, the simultaneous declining of total base cation and nitrate concentrations in stream resulted in very small or insignificant change of ANC from 1992 to 2007. This was also reported in many other study sites, like the Adirondack and Catskill regions (Stoddard et al., 1998; Burns et al., 2006). Some studies have attributed the delay of stream recovery to the loss of base cations from soils (Stoddard et al., 1999; Fölster et al., 2003). In the NDW, base cations except K^+ was found to be depleted from the watershed as observed in Chapter 3. The continuous depletion of Ca^{2+} and Mg^{2+} in the NDW limited the watershed buffer capacity to acid. This indicates that watershed acidification will continue long time until the soil cations are improved and the deposition of S and N is further reduced.

The temporal analysis and model predictions for pH, ANC, sulfate and inorganic nitrogen showed that the NDW watershed has are not recovered from acidification yet, due to declining export of base cations. Stream sulfate concentration remained relatively stable in response to insignificant change of sulfate deposition. Precipitation was the main driver to regulate the output of sulfate as deposition sulfate was diluted at high precipitation and soil adsorption reaction was enhanced during dry season. Stream nitrate was decreasing because of the plant recovery from BWA, even though throughfall deposition of ammonium flux was increasing over

time. Nitrogen export was dependent on vegetation uptake and biotic activity, which was seasonally varied with high retention in summer and low in winter. The continuous depletion of base cations limited watershed buffer capacity to acid anions and led to the lack of watershed recovery from acidification. Since both nitrogen and sulfur are the important acid anions to affect the stream acidification, reduction of atmospheric deposition of these chemicals, especially nitrogen, will determine the speed and extent of the further recovery. A continuous monitoring of atmospheric deposition, stream water chemistry could document future improvements in response to emission reductions (Sullivan et al., 2008).

CHAPTER 5 THE RESPONSE OF STREAM CHEMICAL CONCENTRATIONS AND MASS EXPORT TO BASEFLOW AND STORMFLOW IN A HIGH-ELEVATION WATERSHED OF GREAT SMOKY MOUNTAINS

ABSTRACT

Episodic stream acidification is particular of concern in the Noland Divide Watershed, a high-elevation watershed in the Great Smoky Mountains National Park. Due to poor base cation pools, this watershed is sensitive to acid deposition and liable to be episodically acidified during storm event. The water quality and stream discharge in two streams (southwest and northeast streams) have been monitored since 1991. Based on the hydrographs for the two streams, 125 storm and 493 baseflow samples have been collected during the 17 years (1991 -2007) of data collection. The water chemistry during storm and baseflow were compared to investigate the storm effects to episodic acidification during storm events. Stream pH depression averaged 0.2 pH unit and ANC around 4.5 μeq L^{-1} ANC in both SW and NE streams. The average stormflow ANC of NE stream was 0.6 μeq L^{-1}, which was 6.8 μeq L^{-1} lower than that in SW stream. Compared to SW stream, NE stream was more sensitive to acid deposition and prone to be episodically acidified by storm. Storm events resulted in significant increase of SO_4^{2-}, Ca^{2+} and total Al concentrations, from 28.1 to 35.0 μeq L^{-1} SO_4^{2-}, 47.8 to 50.3 μeq L^{-1} Ca^{2+}, 0.032 to 0.048 mg L^{-1} total Al in SW stream, and from 39.0 to 48.0 μeq L^{-1} SO_4^{2-}, 52.0 to 55.2 μeq L^{-1} Ca^{2+}, 0.047 to 0.069 mg L^{-1} total Al in NE stream. In contrast, NO_3^-, Cl^- and Na^+ concentrations were reduced from 41.6 to 40.1 μeq L^{-1} NO_3^-, 16.0 to 14.0 μeq L^{-1} Cl^-, 26.7 to 23.1 μeq L^{-1} Na^+ in SW stream, and from 46.9 to 44.8 μeq L^{-1} NO_3^-, 19.2 to 15.8 μeq L^{-1} Cl^-, 26.7 to 21.9 μeq L^{-1} Na^+ in NE stream. K^+ and Mg^{2+} were the only ions, which did not show significant change when flow changed from baseflow to stormflow. The ion concentration analysis indicated that the depression of ANC by storm was result of increased SO_4^{2-}, and possibly the increase of organic acid concentration. The relatively stable concentrations of total base cations did not contribute to the change of storm ANC values. The change of chemical concentrations during storm may be attributed to the shift

of flowpath from deep soil flow to shallow flow during storm. Storm water is comprised of throughfall water and shallow soil flow. Consequently, the concentration of one chemical in throughfall can affect its concentration in stream during stormflow. In most years, storms were responsible for the biggest proportion of chemical export, even though storms only accounted for 22% of the total time. The important effects of storms for chemical export and concentration variations in these small streams increases the need to understand of this process in larger watersheds throughout the Park.

Key Words: hydrology; stormflow; baseflow; water chemistry; flowpath; episodic acidification

INTRODUCTION

Hydrological events such as stormflow may contribute substantial amounts of chemical export from the watershed. Recently, stream acidification during peak flow caused more focus and is widespread studied in some sensitive surface waters because aquatic biota are more sensitive to the pulse of environmental stress than chronic acidification (Wigington et al., 1990, 1992; Davies et al., 1992). Many studies found that mass export during storm events significantly contributed to chemical budgets, especially for those which were strongly correlated with stream discharge (Hinton et al., 1997; Swistock et al., 1997). This is especially important in the Noland Divide Watershed (NDW), a high-elevation watershed in the Great Smoky Mountains National Park (GRSM). The predictive models for stream pH, ANC (acid neutralizing capacity), sulfate and nitrate concentrations present in Chapter 4 have already shown that the stream concentrations of chemicals were highly dependent on stream discharge. Negative correlations of pH, ANC and

NO_3^- with discharge, and positive correlation between SO_4^{2-} with discharge, were observed in the NDW streams. Therefore, the changes of stream-flow regimes, such as stormflow and baseflow, should be taken into account to predict stream acidification.

The importance of storms was emphasized in the effect to the depression of acid neutralizing capacity (ANC) (Rice et al., 2004). Episodic acidification was defined when stream ANC was below 0 μeq L^{-1} for some hours or days (Wellington and Driscoll, 2004). Three stream sites in a middle-elevation watershed in the GRSM showed significant depression of ANC to below 0 μeq L^{-1} during peak flow (Deyton et al., 2009). Storm flows generally results in an increase of stream SO_4^{2-} and total Al concentrations (Ohrui and Mitchell, 1999; Mitchell et al., 2006), but has various effects to base cations and nitrate concentration. Base cations and nitrate concentrations are found to be increased in some watersheds, or show some reductions for other basins during storm event (Evans et al., 1999; Wanger et al., 2008; Deyton et al., 2009). High-elevation watersheds are particularly sensitive to the change of hydrology, due to relatively high acid deposition and poor base-cation pools (Deviney et al., 2006; Sullivan et al., 2007).

The change of stream solutes under hydrological events was determined by the dominant flowpath (Wagner et al., 2008). Many studies found that the flowpath was shifted from deeper to shallow subsurface or surface soil during high flow events (Davies et al., 1992; Wigington et al., 1992; Cook et al., 1994). The shift of flowpath is particularly important when shallow soil exhibit different chemical characterizations from deeper soil. Some studies found that sulfate, nitrate and organic acids are found in ghiher concentrations in shallow soils (Kahl et al., 1992; DeWalle and Swistock, 1994; Laudon et al., 2000). Because of the shift of flowpath from deep soil flow to shallow soil flow during rainfall events, a pulse of strong anions is observed in NDW. For some watersheds where higher concentrations of base cation are found in deeper soil layers,

the shift in flowpath will result in dilution of base cations during peak flow (Evans et al., 2007). Both the increase of strong anions and dilution of base cations will contribute to the depression of stream ANC, resulting in episodic stream acidification in sensitive surface waters during a stormflow event.

Given the importance of how hydrology influences the severity of stream acidification, this study is going to analyze the variation of stream chemistries (Cl^-, NO_3^-, SO_4^{2-}, Ca^{2+}, Mg^{2+}, K^+, Na^+, total Al) during baseflow and stormflow to examine if rainfall caused episodic acidification in the NDW. The chemical mass export by baseflow and stormflow were compare to determine which flow type is more important to export of chemical from this watershed.

METHODS

Field Sampling Methods and Laboratory Analysis

Stream discharge from SW and NE streams was monitored at 15 min intervals with float-type stage recorders in stilling wells on 3.0-ft H flumes, located at the NDW watershed exit. The recorded depth was used to calculate stream discharge according to standard H-flume tables in USDA-ARS (1979).The frequency-duration curve during this 17-year study period indicated that occurrence of peakflow and baseflow on SW and NE streams were very similar (Fig. 5-1). Maximum stream discharge was greater in NE stream than SW stream during peakflow period.

Stream samples were collected by manually grabbing from SW and NE stream weekly before 2000, and biweekly since then. Once samples were taken back to laboratory, pH, ANC and conductivity were measured by autotitrator within 24 hours. After that, samples were kept at 4^oC until chemical analysis. Samples filtered by 0.4-μm membrane and analyzed for SO_4^{2-}, NO_3^-, Cl^-, and NH_4^+ by ion chromatography; and Ca^{2+}, Mg^{2+}, K^+, Na^+ by atomic absorption spectrometry

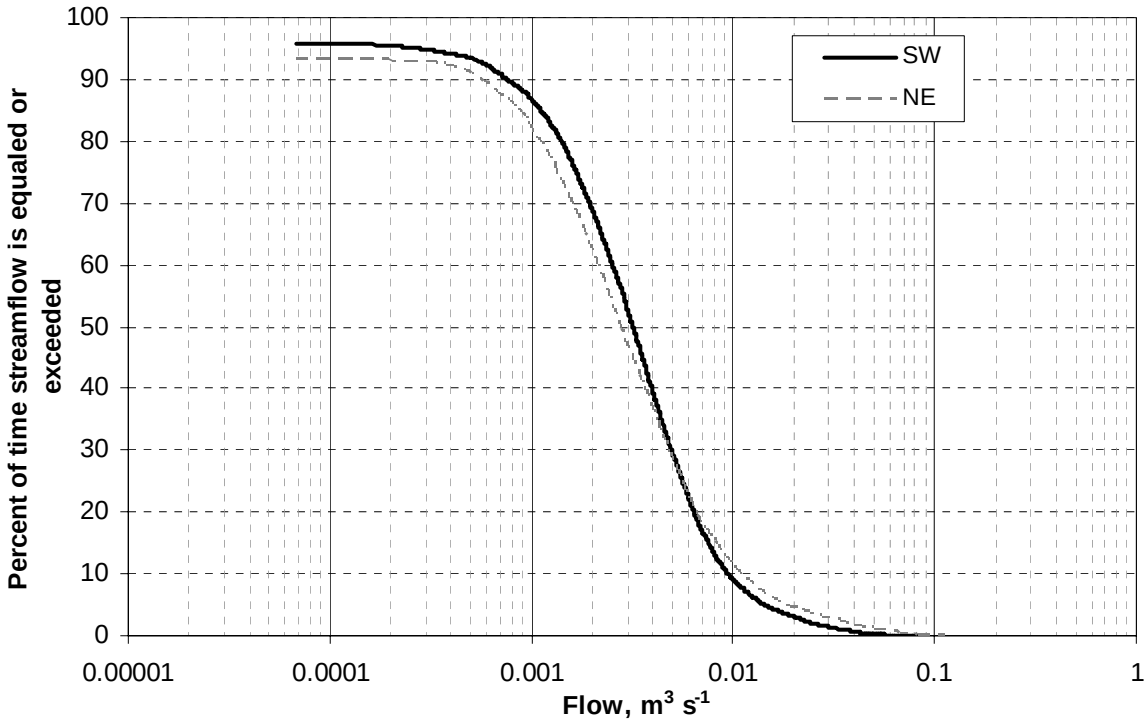

Fig. 5-1. Flow-duration curves for SW and NE streams based on 15-minutes data from late 1991 to 2007.

(1991-1993, 1998-2003) and inductively-coupled plasma spectrometry (2003-2006). From 1993 to 1998, Na^+ and K^+ were measured by ion chromatography, but Ca^{2+} and Mg^{2+} were not measured. The quality assurance/quality control (QA/QC) criteria were met through sample spikes, replicates and U.S. Geological Survey known samples with every set of samples.

Hydrograph Separation for Baseflow and Stormflow

Stream flow was separated into stormflow and baseflow by the hydrograph separation method proposed by Hewlett and Hibbert (1967). A stormflow began when a significant increase of stream discharge was observed, and ended if the receding limb of the hydrograph was intersected with a line which was drawn from the baseflow and had a slope of 0.00546 L s^{-1} ha^{-1} hr^{-1} (Fig. 5-

2). Although the hydrograph method is arbitrary, it provides a consistent method to define stormflow and baseflow.

According to the hydrograph separation criteria, 125 samples were grabbed during stormflow and 493 samples were collected during baseflow for total 618 water samples collected during this 17-year study period. The baseflow and stormflow events were evenly distributed during the monitoring years from 1991 to 2007, to eliminate any variations caused by the temporal trend of chemical concentrations and fluxes. In addition, seasonal variations were also eliminated by collecting stormflow and baseflow samples in all months. However, most stormflow occurred from November to April while most baseflow samples were collected from May to October because winter is the wet season and summer is the dry season in this region.

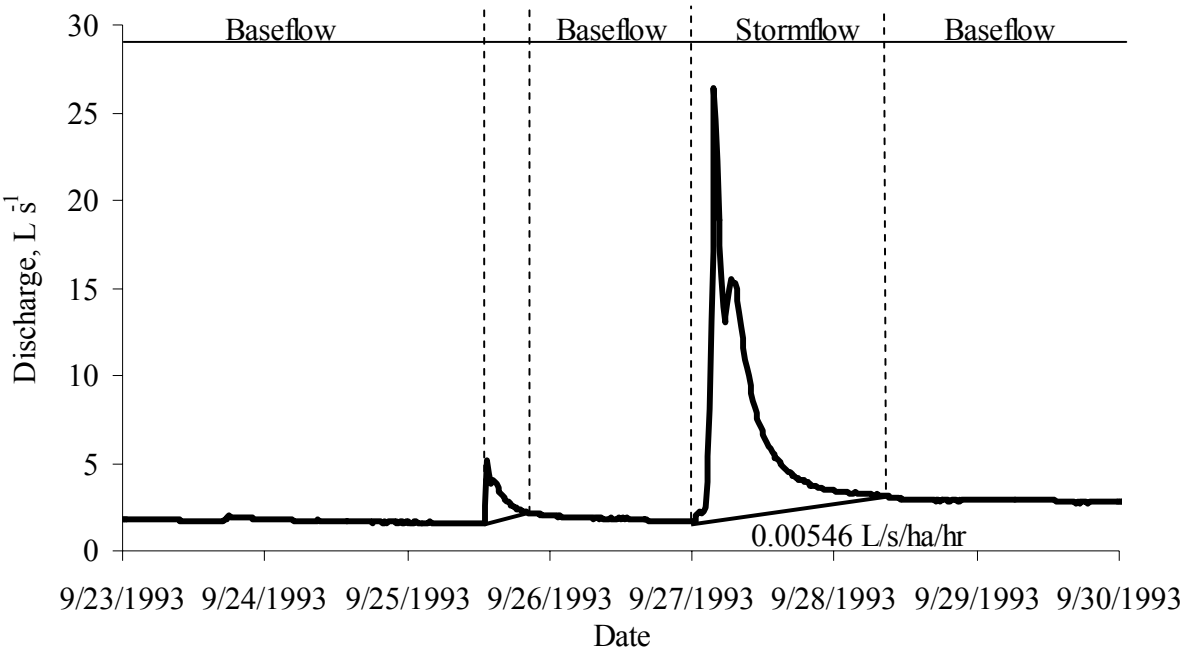

Fig. 5-2. The schematic graph to define baseflow and stormflow by hydrograph separation method using the SW stream discharge from September 23 1993 to September 30 1993.

Data Analysis

Annual stream chemical fluxes in stormflow were calculated by using the average concentration to multiple the discharge during stormflow to get the storm mass export. Similarly, average baseflow concentration was multiplied with the baseflow discharge in one year to obtain annual stream flux in baseflow. The concentration standard deviation was used to be multiplied with discharge to represent the flux standard deviation.

The average chemical concentrations during baseflow and stormflow were compared by analysis of variance (ANOVA) using a significance $p \leq 0.05$. Statistical analyses were performed by JMP 8.0.1.

RESULTS

Stream Discharge

From November of 1991 until 2007, total 1,179,733 m^3 of baseflow water and 1,322,485 m^3 of stormflow water was exported from NDW through the SW stream, and 1,187,708 m^3 baseflow water and 1,853,889 m^3 stormflow water was discharged from the NE stream (Table 5-1). Approximately 53% of water in SW stream and 61% of water in the NE stream were exported from the watershed during storm events even through strom flows only accounted for 22% of total time. Every year stream flow was dominated by baseflow for more than 250 days of the 365 days. In 2007, a drought year, baseflow exported around 4% more water than stormflow. In contrast, 1994 was the wettest year of record and more than 63% of the water exported from the watershed occurred during stormflow event.

Characterization of Baseflow and Stormflow Chemistry

Significant depression of pH and ANC in the SW and NE streams during stormflow was observed (Table 5-2). Average baseflow pH for SW stream was 5.9 and average stormflow pH was 5.7. A similar pattern was observed in the NE stream, which had average baseflow pH of 5.6 and a stormflow pH of 5.4. Similarly, average ANC dropped from 12.6 μeq L^{-1} to 7.4 μeq L^{-1} in the SW stream, from 4.8 μeq L^{-1} to 0.6 μeq L^{-1} in the NE stream for baseflow and stormflow respectively.

Sulfate, calcium and alumina were the only chemicals to display a significant increase in stream concentration during stormflow (all $p < 0.05$). The average concentrations of SO_4^{2-}, Ca^{2+} and total Al in SW stream were elevated from 28.1 to 35 μeq L^{-1}, from 47.8 to 50.3 μeq L^{-1}, and from 0.032 to 0.048 mg L^{-1} during baseflow and stormflow respectively (Table 5-2). In NE stream, the average concentrations were increased from 39.0 to 48.0 μeq L^{-1} for SO_4^{2-}, from 52.0 to 55.2 for Ca^{2+} μeq L^{-1}, and from 0.047 to 0.069 mg L^{-1} for total Al.

In contrast, stormflow concentrations of NO_3^-, Na^+ and Cl^- had significantly lower values than baseflow concentrations. The average baseflow concentrations were 41.6 μeq L^{-1} NO_3^-, 16.0 μeq L^{-1} Cl^- and 26.7 μeq L^{-1} Na^+ in SW stream, and 46.9 μeq L^{-1} NO_3^-, 19.2 μeq L^{-1} Cl^- and 20.7 μeq L^{-1} Na^+ in NE stream (Table 5-2). In stormflow, these values were decreased to be 40.1 μeq L^{-1} NO_3^-, 14.0 μeq L^{-1} Cl^- and 18.8 μeq L^{-1} Na^+ in SW stream, and 44.8 μeq L^{-1} NO_3^-, 15.8 μeq L^{-1} Cl^- and 21.0 μeq L^{-1} Na^+ in NE stream.

K^+ and Mg^{2+} concentrations remained relatively stable regardless of stream flow. The average concentrations of K^+ and Mg^{2+} were around 8.5 and 18.6 μeq L^{-1} in SW stream, and about 11 and 21 μeq L^{-1} in NE stream. NH_4^+ had relatively low concentrations, mostly below 1.0 μeq L^{-1} in both streams.

Table 5-1. Summary of stormflow and baseflow discharge and the number of event days from November 1991 to 2007, based on 15-minute in-situ record.

Year	SW					NE				
	Baseflow		Stormflow		Days Missing observation	Baseflow		Stormflow		Days missing observation
	Annual total Discharge,m^3	Number of days	Annual total Discharge,m^3	Number of days		Annual total Discharge,m^3	Number of days	Annual total Discharge,m^3	Number of days	
1991	8,887	41	28,417	14	0	10,502	41	52,698	14	0
1992	92,487	289	92,334	77	0	93,282	289	120,887	77	0
1993	66,979	295	72,234	64	6	57,660	295	76,797	64	6
1994	75,660	259	129,145	105	1	72,596	259	192,214	105	1
1995	60,975	246	80,775	79	41	75,368	246	117,742	79	41
1996	87,874	280	85,206	81	5	104,423	280	143,633	81	5
1997	68,651	271	89,296	93	1	69,986	271	152,517	93	1
1998	87,874	280	85,206	81	4	104,423	280	143,633	81	4
1999	58,837	275	69,278	67	23	70,793	279	122,370	72	15
2000	53,819	280	56,918	63	23	59,075	297	89,846	69	0
2001	72,200	291	62,928	74	0	60,185	291	90,268	74	0
2002	80,806	279	86,807	86	0	73,804	279	121,662	86	0
2003	91,076	275	101,824	90	0	80,472	275	142,509	90	0
2004	74,811	265	89,712	75	25	75,550	265	89,567	75	25
2005	70,290	270	60,009	72	23	54,634	253	56,852	60	52
2006*	70,820	264	80,740	97	4	70,253	260	90,280	102	3
2007*	57,687	299	51,655	60	6	54,702	299	50,414	60	6
Sum	1,179,733	4459	1,322,485	1277	162	1,187,708	4459	1,853,889	1281	159

* Around half year observation data in 2006 and 2007 were missed due to field equipment malfunction. The missing data were supplemented by WinHSPF model prediction.

Table 5-2. Baseflow and stormflow water quality data for SW and NE streams in the NDW by using observations from 1991 to 2007. Units at μeq L^{-1}, except pH at pH unit, and Al at ppm. ANOVA significance levels, $p < 0.05$.

			pH	ANC	Cl^-	NO_3^-	SO_4^{2-}	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}	Al	BC*	AN**
SW	Baseflow	Mean	5.9	12.6	16.0	41.6	28.1	0.8	26.7	8.5	18.6	47.8	0.032	101.4	85.8
		SD	0.2	7.0	9.1	6.4	4.2	2.5	5.5	5.6	2.8	4.7	0.028	11.6	12.3
		n	487	484	486	487	487	487	487	486	265	265	83	264	486
	Stormflow	Mean	5.7	7.4	14.0	40.1	35.0	0.5	23.1	8.6	18.8	50.3	0.048	101.1	89.0
		SD	0.3	7.7	7.9	8.2	5.8	1.3	4.8	3.2	3.2	5.5	0.043	11.2	13.6
		n	125	125	125	125	125	125	125	125	65	65	23	65	125
	ANOVA	p-value	<0.01	<0.01	0.02	0.02	<0.01	0.19	<0.01	0.93	0.57	<0.01	0.04	0.84	0.01
NE	Baseflow	Mean	5.6	4.8	19.2	46.9	39.0	1.0	26.7	11.6	20.7	52.0	0.047	111.3	105.2
		SD	0.2	5.7	11.4	7.7	5.5	2.1	7.0	8.1	2.9	5.6	0.023	17.6	15.7
		n	488	484	487	487	487	481	487	485	252	252	80	250	487
	Stormflow	Mean	5.4	0.6	15.8	44.8	48.0	0.5	21.9	11.0	21.0	55.2	0.069	109.3	108.6
		SD	0.3	6.2	8.6	9.1	8.1	1.3	4.0	4.1	3.9	10.0	0.045	15.5	15.7
		n	125	125	125	125	125	125	125	125	55	56	24	55	125
	ANOVA	p-value	<0.01	<0.01	0.00	0.01	<0.01	0.01	<0.01	0.38	0.47	<0.01	<0.01	0.61	0.03

* BC = sum of base cations (Na^+, K^+, Mg^{2+}, Ca^{2+})
**AN = sum of anions (Cl^-, NO_3^-, SO_4^{2-})

The flow change from baseflow to stormflow had no significant effect to SW stream, where NH_4^+ concentration was 0.8μeq L^{-1} in stormflow and 0.5μeq L^{-1} in baseflow. However, a significant reduction of 0.5 μeq L^{-1} NH_4^+ was observed in NE stream when flow changed from baseflow to stormflow.

Due to the inverse changes of Na^+ and Ca^{2+} concentrations, and relatively stable K^+ and Mg^{2+} concentrations during stormflow and baseflow, the total base cations concentrations did not show significant change, and remained around 101 μeq L^{-1} in SW stream and 110 μeq L^{-1} in NE stream at both hydrological events. Compared to base cations, the sum of anions was increased from 85.8 to 89.0 μeq L^{-1} in SW stream, and from 105.2 to 108.6 μeq L^{-1} in NE stream. This change indicated that the episodic acidification was caused by increased anions concentration, instead of reduction of base cations concentration in the NDW.

Stream Net Export of Chemicals

Due to the difference of stream flow and the chemical concentrations during stormflow and baseflow, the annual mass export of each chemical by stream varied at different flow period. In general, NE stream can export more SO_4^{2-}, NO_3^-, Ca^{2+}, Mg^{2+} and K^+ than SW stream in both hydrological events (Fig. 5-3). The effect of storm to solute export from this watershed was significant, since more than 50% of those ions flux were exported by stormflow in most years. The difference of mass output between stormflow and baseflow was especially significant in NE stream, where SO_4^{2-} load by storm was approximately 2 times of baseflow load.

During this 17-year study period, around 1,500 ~ 3,000 eq yr^{-1} SO_4^{2-} flowed out of the NDW watershed by stormflow and baseflow through SW stream (Fig. 5-3). Compared to SW stream, NE stream carried similar amount of SO_4^{2-} by baseflow, but about double amount of SO_4^{2-} by stormflow. This mass export was dominated by stormflow, which could carry 700 eq yr^{-1} and

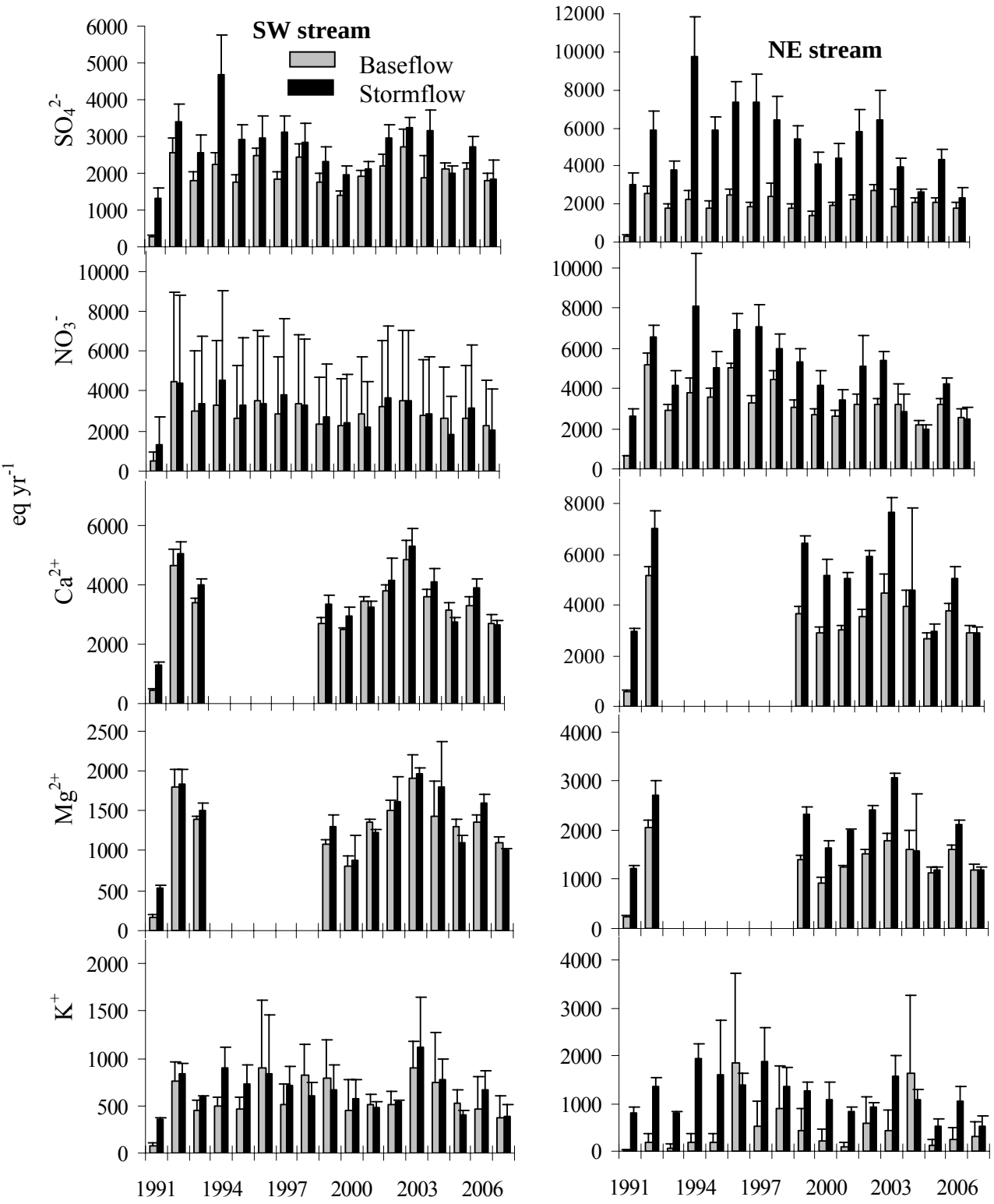

Fig. 5-3. Annual stream mass export of NO_3^-, SO_4^{2-}, Ca^{2+}, Mg^{2+} and K^+ by baseflow and stormflow through SW and NE stream from 1991 to 2007. Ca^{2+} and Mg^{2+} were not measured during 1994 to 1997.

2,500 eq yr^{-1} more SO_4^{2-} averagely by SW and NE streams, respectively. Due to significant great stormflow discharge in 1994, stormflow exported around two times SO_4^{2-} mass of that by baseflow in that year.

From 1992 to 2007, NO_3^- export was around 2,000 ~ 4,000 eq yr^{-1} and over 3,000 eq yr-1 through SW and NE streams in both stormflow and baseflow periods (Fig. 5-3). For most years, stormflow could carry more NO_3^- than baseflow. The stream mass export of NO_3^- showed great variation during study period, probably due to non-linear biogeochemical processes in the watershed.

For Ca^{2+} and Mg^{2+}, the amount of mass exported by stormflow was slightly greater than those by baseflow, which could carry over 3,000 eq yr^{-1} Ca^{2+} and over 1,000 eq yr^{-1} Mg^{2+} (Fig. 5-3). The stream load of K^+ varied from year to year, averagely over 500 eq yr^{-1} in SW stream and 200 eq yr^{-1} in NE stream.

DISCUSSION

The water sample collection in this study area was a routine for the study site, hence no additional effort was necessary to collect samples specifically at stormflow or baseflow. Since stormflow samples were generally not collected exactly at peakflow, the event chemical concentration may differ from the average concentration during one hydrological event. In addition, not all storm samples were collected. Therefore, the calculation of mass export through stream should contain some uncertainties. Besides the direct calculation of mass export, the concentration difference between stormflow and baseflow could give some implications of the mass export amount. Since more than 50% of water was discharged as storm, one chemical with higher concentration or insignificant changes of concentration in storm was expected to be

exported mainly by stormflow. Significant higher concentrations of SO_4^{2-}, Ca^{2+}, and the insignificant concentration changes of Mg^{2+} and K^+ during storm event indicated that the stream export of those chemicals were dominated by storm.

The change of stream solutes during hydrological events was attributed to the shift of flowpaths, resulting in the change of stream components. Stormflow was identified to be composed of shallow groundwater at the start of the event, throughfall on the hydrograph rising limb and valley-bottom riparian water at the receding limb of the streamflow hydrograph (Inamdar and Mitchell, 2006). This components mixture model indicated that throughfall and subsurface flow gave great proportion during storm event. The average throughfall concentrations for pH, ANC, SO_4^{2-}, NO_3^- were 4.3, -48.9 μeq L^{-1}, 81.8 μeq L^{-1} and 38.8 μeq L^{-1}, respectively. The difference of stream and throughfall concentrations resulted in the increase or decrease of chemical concentrations when flow changed from baseflow to stormflow.

It was widely reported that storm events usually had greater sulfate concentration than the corresponding baseflow values (Inamdar et al., 2006; Mitchell et al., 2006). Some studies attributed the increase of SO_4^{2-} during storm-event to the mobilization of accumulated SO_4^{2-}, which was previously oxidized from organic sulfur during drought (Mitchell et al., 2008). Due to the increase of water table, those stored SO_4^{2-} was flushed into stream, resulting in the elevation of SO_4^{2-} concentration. However, sulfate concentrations in soil water was found to be uniform from shallow to deeper soil horizons, thus the increase of water table during peak flow cannot affect the stream sulfate concentration. Elevated stream sulfate concentration during stormflow may be explained by the high throughfall deposition concentration of sulfate. The average sulfate concentration in throughfall was 81.8 μeq L^{-1}, around two times greater than the stream

concentration. As a result, stream sulfate concentration was elevated in response to the input of throughfall water.

The source of nitrate was biological driven since significant high nitrate concentration converted from organic nitrogen by mineralization and nitrification process was observed in shallow soil layer. During a storm event, throughfall water with low nitrate concentration diluted the stream water, resulting in the reduction of stream nitrate concentration when flow shifted from baseflow to stormflow.

The reduction of pH during storm event could expedite weathering process and alumina dissolution. Therefore, the increase of base cations concentrations was expected. It was reported that forest floor contributed significant input of stream Al (Palmer et al., 2005). Total Al was significant correlated with stream pH, indicating the increase of stream Al was resulted from the reduction of pH during storm event. Calcium was the only base cation showing increasing trend during storm, probably because soil content of Ca^{2+} was rich than other base cations. Na^{+} content in soil was lower than other base cations. As a result, the dilution of storm contributed to the reduction of Na^{+} concentration. The dilution factor can be calculated by using concentration in storm to divide that in baseflow. For both Na^{+} and Cl^{-}, it was found that the dilution factors in SW stream were around 0.87 and 0.82 in NE stream. The ratio of stormflow concentrations to baseflow concentrations for all other studied ions, except NH_4^{+}, were greater than this dilution factors, suggesting that storm export more mass in unit time than those by baseflow.

Episodic acidification was defined when stream ANC was below 0 μeq L^{-1} for short time (Wellington and Driscoll, 2004). Although the average baseflow and stormflow ANC values were greater than 0 μeq L^{-1}, those values were easy to drop below 0 μeq L^{-1}, especially in NE stream. ANC was expressed by the difference of total base cations and total anions. In current

study, the sum of Cl^-, SO_4^{2-} and NO_3^- was used to represent total anions. The magnitude of this difference was greater than real ANC, implying other anions such as organic acid, was contributing to reduce stream ANC. Some studies attributed the depression of ANC to the dilution of base cation concentrations during stormflow (Davies et al., 1992; Wigington et al., 1992). However, the insignificant change of base cation concentrations ($p = 0.84$ for SW stream, $p = 0.60$ for NE stream) indicated that the dilution of base cation concentrations during stormflow did not contribute to the reduction in ANC in this watershed. The average concentrations of K^+ and Mg^{2+} did not show significant change from baseflow to stormflow for both streams, whereas significant high Ca^{2+} and low Na^+ concentrations were found in storm. A study of episodic stream acidification for three stream sites at middle elevation of the GRSM found that stormflow base cations concentrations were increased during stormflow events from baseflow (Deyton et al., 2009). This finding also indicated that dilution of base cations was not the main driver to reduce stream ANC. Therefore, the depression of ANC had to be attributed to the increase of sulfate during high flow events. In addition, the increase of organic acid, which was not studied here, was also found to play an important role to lower stream ANC during stormflow events (Deyton et al., 2009). These elevated anion concentrations resulted in NE stream ANC to be reduced to below zero, the most severe level of acidification during some stormflow event.

The 17-year monitoring data of SW and NE streams water quality in the high-elevation NDW showed that storm had significant effect to chemical mass export and concentration variation. More than 50% of water in less than 22% of total time was exported in form of storm. Consequently, mass export of studied chemicals was dominated by stormflow in both streams. The shift of flowpath and the chemical concentrations in throughfall deposition resulted in

elevated SO_4^{2-}, Ca^{2+} and total Al concentrations with depression of pH, ANC and NO_3^- concentration during storm event. The mixture of throughfall water into stream was a great contributor to the water quality change. Even though in one watershed, the export mechanism for all solutes were not necessary consistent (Wanger et al., 2008). Total Al was highly determined by stream pH, rather than by throughfall deposition. Due to the depression of ANC, resulted from increased sulfate concentration and stable total base cations concentration, episodic acidification could be observed in this watershed. The results provided in this study showed the effects of storm to mass export and ion concentrations variation in high-elevation watershed, which could aid the management to better understand the watershed response to different hydrological event

CHAPTER 6 SOIL ACID-BASE CHEMISTRY OF A HIGH-ELEVATION WATERSHED IN THE GREAT SMOKY MOUNTAINS NATIONAL PARK AFFECTED BY LONG-TERM ACID DEPOSITION

This chapter is a slightly revised version of a manuscript with the same title submitted to the *Journal of Environmental Quality* by Meijun Cai, Amy M. Johnson, John S. Schwartz, Stephen E. Moore, and Matt A. Kulp.

ABSTRACT

Understanding the acid-base chemistry of soil and the soil processes related to the release or retention of sulfate and nitrate is important in order to predict watershed recovery from long-term acid deposition. Soils were sampled from the Noland Divide Watershed (NDW), a small, high elevation watershed in the Great Smoky Mountains National Park receiving high rates of acid deposition. Soil samples were measured for chemical properties related to acidification, and used to conduct sulfate adsorption and nitrogen (N) incubation experiments. Shallow soil was highest in acidic and basic ions than deeper soils, and the mean effective cation exchange capacity was 7.87, 4.98 and 3.52 $cmol_c\ kg^{-1}$ in the A, Bw and Cb horizons, respectively. In all three soil horizons, the base saturation was below 4% and the ratio of Ca/Al was below 0.001, indicating that the NDW is very sensitive to acid deposition. Based on results from sulfate adsorption isotherms, the NDW has not reached its maximum sulfate saturation and is likely able to accumulate further additions of sulfate. Desorption of sulfate from NDW soils is expected if sulfate concentrations in soil solution drop below 50 $\mu eq\ L^{-1}$. The adsorption and desorption of sulfate was highly dependent on pH and organic carbon content, showing a high adsorption capacity at low soil pH and organic carbon contents. Soil organic N was 500 times greater than inorganic N in the A soil horizon, providing a sufficient N source for mineralization and nitrification processes in the A soil horizon. As a result, soil net mineralization and nitrification

rates remained constant during a 28-day incubation period. Mean net mineralization and nitrification rates were much lower in the Bw and Cb horizons and decreased over time, probably related to lower organic matter contents. Results suggest that nitrate export from the watershed is controlled by biological mechanisms rather than by nitrate deposition. The results from this study provide a missing component of the overall understanding of watershed processes affecting ecosystem response to future changes in acid deposition.

Key Words: soil characteristics, base cations, aluminum, sulfate adsorption, nitrogen mineralization, nitrification, acidic deposition, southern Appalachian

INTRODUCTION

Ecosystem deterioration from long-term acid deposition is of great concern to resource managers in the Great Smoky Mountains National Park (GRSM) as it has received some of the highest acid deposition rates in North America (Nodvin et al., 1995; Shubzda et al., 1995; NADP, 2006). High elevation watersheds in the GRSM and elsewhere in the eastern United States have been shown to be especially sensitive to acidic inputs due to a low capacity to buffer changes in acidity as evidenced by low stream pH and acid neutralizing capacity (ANC) (Silsbee and Larson, 1982; Johnson and Lindberg, 1992; Robinson et al., 2008). The Noland Divide Watershed (NDW), a high-elevation watershed in the GRSM, has historically received high rates of nitrate and sulfate via precipitation and has been shown to be sensitive to acidic inputs. In a recent study examining water quality in the NDW, stream pH and ANC levels were below 6.0 and 20 μeq L^{-1},respectively, levels that are indicative of a severe level of stream acidification (Driscoll et al.,

2001). This condition can potentially have adverse effects on stream biota and is thought to be responsible for the extirpation of native brook trout from some streams in the GRSM (Robinson et al., 2008).

In the last few decades depositional inputs of nitrogen (N) and sulfate have decreased significantly in the US due to the Clean Air Act regulations (Driscoll et al., 1998; Stoddard et al., 1999). However, corresponding improvements in stream chemistry have been insignificant in some acid-impacted watersheds including the NDW, a result that has been attributed to the long-term depletion of base cations from soil, desorption of previously sorbed soil sulfate, and biological transformations of soil N (Manderscheid et al., 2000; Sullivan et al., 2006). This emphasizes the need to better understand the soil processes occurring in acid-impacted ecosystems and how they ultimately affect stream health. Input-output budgets can be useful in evaluating the condition of watersheds or changes over time, but attempting to link atmospheric processes directly to stream quality without considering soil nutrient cycling ignores an important component of the system and prevents a complete understanding of ecosystem response to acid deposition (Lawrence, 2002). Unfortunately, characterization of acid-base chemistry of soils has generally not been as thoroughly studied as stream chemistry in many acid-affected watersheds (Sullivan et al., 2006). This lack of data also precludes the use of model simulations to predict watershed response to future reductions in acid deposition (Helliwell et al., 1998).

The major effects of long-term acid deposition on soils include depletion of base cations, mobilization of aluminum and accumulation of sulfate and nitrate (Castro and Morgan, 2000; Driscoll et al., 2001). Depletion of soil base cations is thought to be caused by a number of factors related to enhanced input of acid anions and low pH. The lower cation exchange capacity

resulting from decreased pH, the displacement of base cations from the soil exchange complex by Al^{3+}, and the bases acting as counterions to balance leached SO_4^{2-} and NO_3^- all increase the susceptibility of base cations to leaching (Cronan and Schofield, 1990; Likens et al., 1996; Blake et al., 1999; Fernandez et al., 2003). Reductions in pH and base saturation from inherently low-base soils leads to stream acidification as evidenced by decreases in stream pH and ANC throughout the eastern US (Lawrence, 2002; Driscoll et al., 2003; Sullivan et al., 2008). In addition, enhanced mobilization of soil Al in watersheds having low base saturation and high inputs of acid pollutant can cause high concentrations of Al in streams that are potentially toxic to aquatic biota (Cronan and Schofield, 1990; Driscoll et al., 2003).

Sulfate and nitrate are the dominant acid-forming anions associated with acid deposition and their fate can greatly influence watershed acidification by controlling cation mobility and leaching. Chemical and biological processes occurring in soils can cause retention of these anions, thus limiting their immediate export to streams and potentially delaying watershed recovery (Lawrence, 2002). In a synthesis of trends in acid recovery of northern and eastern U.S. forests over the past 20 years, Kahl et al. (2004) found that streams draining southeastern forests have not shown immediate responses to decreases in sulfate deposition while northeastern forests have shown significant reductions in stream sulfate concentrations. These findings are thought to be due to the enhanced potential for sulfate adsorption/desorption in southeastern soils. Sulfate cycling in forest soils of the Southeast is predominately controlled by adsorption/desorption reactions which regulate the retention and release of sulfate to surface waters (Martinson et al., 2003). As atmospheric deposition of sulfate decreases, it is possible that adsorbed sulfate will slowly desorb and continue to contribute to acidic stream conditions for many years (Sullivan et al., 2008). Soil adsorption of sulfate is highly dependent on soil pH and, to a lesser extent,

organic carbon (C) content. In general, studies examining sulfate sorption behavior have found that sulfate adsorption increases as pH decreases from 5.5 to 4.0, and approaches a constant level of absorption at pH below 4.0 (Nodvin et al., 1986; Courchesne and Hendershot, 1990; Pigna and Violante, 2003). Thus, as acidity increases the potential for soils to retain sulfate is enhanced. On the other hand, the presence of organic C in acid forest soils may act to reduce adsorption of sulfate due to competition for positively charged binding sites (Comfort et al., 1992; Kooner et al., 1995; Kaiser and Zech, 1996).

Long-term depositional inputs of N to forested ecosystems can contribute to stream acidification by increasing nitrate export and by causing shifts in biological transformations including enhanced nitrification, referred to as N-saturation (Koopmans et al., 1995; Nodvin et al., 1995). Decreases in N deposition have not been as significant as recent decreases in sulfate for a number of reasons (Kahl et al., 2004). Deposition of N, unlike S, involves multiple sources and oxidation states of N. Nitrogen pollution from power plants, generally deposited as nitrate is the only source covered in current legislation. However, even where nitrate deposition has been found to be decreasing, such as in areas of the Northeast, watershed export of nitrate has not shown a significant declining trend (McNulty et al., 1990; Ollinger et al., 1993; Stoddard et al., 1999). This is likely due to the complex dynamics of N that exist in forested soils. Nitrogen in forested ecosystems is strongly controlled by biological processes including uptake by soil microbes and plants, mineralization of organic N and nitrification. Therefore, changes in the rates of biological N transformations will affect watershed recovery from acidification as much as, if not more than, changes in nitrate deposition (Koopmans et al., 1995). In addition, the rates of N transformations are much more variable over soil depth, elevation and forest types than other chemical measurements related to acidification (Persson and Wirén, 1995, Fernandez et al.,

2000; Jefts et al., 2004). The biological and chemical interactions occurring in N-saturated forest ecosystems and how these affect long-term stream acidity are still relatively unknown.

In order to gain a better understanding of the biogeochemical processes involved in ecosystem recovery from long-term acid deposition, it is imperative to examine the role of soil in the retention and release of acidic and basic ions to surface waters. If predictive models are to be used to estimate future environmental scenarios, soil chemistry data, which has previously been lacking, will be needed. Therefore, the specific objectives of this study were: 1) to characterize the acid-base chemistry of soils in the NDW at different elevations and in various soil horizons; 2) to describe the retention behavior of sulfate in NDW soils at different pH levels; and 3) to investigate the potential biological transformation of N occurring in NDW soils.

MATERIALS AND METHODS

Sample Collection

Four sampling sites were selected throughout the watershed to represent the elevation gradient: NS1 located at the highest elevation (1900 m), NS2 located approximately 20 m above Clingmans Dome Road, NS3 located approximately 20 m below Clingmans Dome Road, and NS4 located adjacent to the stream outlet at the lower end of the watershed (Fig. 2-1). The sample sites reflect the change of elevation from highest to lowest while avoiding the effect of the paved road which bisects the watershed. Soil samples were collected from each of the four sites (NS1-NS4) in June, August, and November of 2008 and March of 2009 in order to eliminate any seasonal differences. Previous research on this site has shown chemical properties related to long-term acid deposition differ by soil horizon. The high organic matter A horizon has been previously shown to have greater net nitrification and N mineralization rates, resulting in

higher nitrate concentrations and lower pH in the this horizon. Therefore, the soil was sampled by soil horizon (A, Bw, and Cb) in order to examine any differences occurring due to soil horizonation. To avoid the effect of antecedent precipitation, at least two continuous dry days were required before field sampling. Soil cores were taken randomly at each sample location and samples from the same soil horizon were composited. Soil samples were transported to the University of Tennessee Water Quality Laboratory where they were stored at 4°C until analysis was performed.

Laboratory Analysis

Soil samples were air-dried at 4^{o}C overnight and passed through a 2-mm sieve to remove gravel, leaf debris, and soil material larger than 2mm. All laboratory analyses were replicated three times on each sample for QA\QC purposes.

Soil moisture was determined gravimetrically by drying a 5-g soil sample at 105^{o}C (Hart et al., 1994). Soil pH was measured in a 1:1 soil: solution of water. Exchangeable bases and exchangeable Al were measured by extraction with an unbuffered 0.2 M NH_4Cl solution and analysis by inductively coupled plasma spectroscopy (ICP) (Sumner and Miller, 1996). Total exchangeable base was expressed as the sum of measured base cations (Ca^{2+}, Mg^{2+}, K^{+}, and Na^{+}). Exchangeable acidity was determined by extraction with 1M KCl followed by titration with 0.1M NaOH and phenolphathalein indicator (Sims, 1996). Exchangeable H^{+} concentration was calculated as the difference between total exchangeable acidity and exchangeable Al. The effective cation exchange capacity (CEC_e) was calculated as the sum of exchangeable base cations and exchangeable acidity. Base saturation was taken as the percentage of the CEC_e occupied by exchangeable bases. Exchangeable sulfate, nitrate and ammonium were measured by extraction with 0.5 mM KCl and analysis by ion chromatography (IC) (Cronan and Schofield,

1990; Stams and Marnette, 1990). Total sulfate was determined by extraction with 1 mM $Ca(H_2PO_4)_2$ and analysis by IC (Tabatabai, 1996). Organic N was determined by measuring total Kjeldahl N and subtracting the ammonium concentration. Total Kjeldahl N was measured by digestion with a $K_2SO_4/CuSO_4$ catalyst and sulfuric acid followed by analysis of ammonium on an flow injection autoanalyzer (Hach, 2005).

Sulfate Adsorption

In order to examine the effect of pH on the level of potential sulfate desorption from NDW soils, soil from the NS4 site was extracted with KCl at six different pH levels (4.25, 4.33, 4.41, 4.62, 5.15, 5.63). Adsorption isotherms were also prepared by batch experiments using soil samples from the A, Bw and Cb horizons of the NS4 site only at six sulfate concentrations (0, 50, 100, 200, 300, 400 $\mu eq\ L^{-1}$) and three pH levels (4.0, 4.4, 5.0). These levels of pH were chosen because they represented the approximate range of pH measured in soils from the sample sites. Additionally, sulfate adsorption has been shown to reach a maximum at pH 4.0 (Nodvin et al., 1986; Martinson and Alveteg, 2004). Initial sulfate solutions were prepared by dissolving Na_2SO_4 in deionized water. A 4-g sieved (2-mm diameter) soil sample from each soil horizon was mixed with 40 ml sulfate solution and the pH adjusted with the addition of 0.1 M HCl or 0.1 M NaOH. The solutions were shaken for 24 hr at 200 rpm on a reciprocating shaker. After this period of equilibration, the slurry solutions were centrifuged at 5,000 rpm for 10 min. The supernatant was filtered through a 0.4 μm membrane filter and was analyzed for sulfate by IC.

Sulfate sorption equations were expressed in the form of the Langmuir and Freundlich models (Johnson et al., 1993; Kros et al., 1995; Martinson et al., 2003). Both models were employed to fit the adsorption results to find the best fit.

The Langmuir model is given by:

$$Q = \frac{Q_{\max} KC}{1 + KC}$$

where Q is the amount of sulfate adsorbed on the soil surface at equilibrium; C is the equilibrium concentration; K is the equilibrium constant; Q_{max} is the maximum amount of sulfate that can potentially be adsorbed to the soil surface.

The Freundlich model is expressed by:

$$Q = mC^n$$

where Q is the same as above and m and n are empirical constants.

Mineralization and Nitrification Incubations

To determine net N mineralization and nitrification rates, a 50 g soil sample containing approximately 30% moisture was placed in a plastic cup, covered with aluminum foil which was perforated for ventilation, and incubated in the dark at ~22^{o}C for 7, 14, and 28 days. At the end of each incubation period, a 5-g subsample of the incubated soil taken was extracted with 50mL of 0.5 mM KCl, filtered, and frozen until analysis of NH_4^+ and NO_3^- by IC (Jefts et al., 2004). A pre-incubation sample was also analyzed to represent time zero.

The net mineralization rate was calculated as the change in total inorganic N ($NH_4^+ + NO_3^-$) during the incubation period divided by the number of days incubated. The net nitrification rate was determined by the change in nitrate concentration divided by the incubation period (Persson and Wirén, 1995).

Data Analysis

The soil concentration of the measured ions was expressed as μeq kg^{-1} dry soil. For most ions, measured data can be easily converted from mg to μeq by using the molar weight. However, the species, and thus charge, of Al is highly dependent on solution pH. Therefore, the conversion of

Al from mg to μeq requires knowledge of the distribution of Al species present under a given set of conditions. To this end, the average charge of Al was calculated using the PHREEQC geochemical equilibrium model.

Mean values of each measured soil parameter were compared across seasons, elevations, and soil horizons by using the Tukey's HSD method in JMP. Significance was determined by a p-value below 0.05.

RESULTS

Soil Characterization

Results for measured soil chemical parameters from NDW are presented in Table 6-1 including exchange ions, total sulfate and total organic N. Besides soil N, which increased with increasing elevation, results did not differ across elevation or season and, therefore, data is presented as an average of all sampling sites and sampling times. Most soil chemical properties decreased in deeper soil horizons, with the A horizon having the greatest concentrations and the lowest concentrations occurring in the Cb horizon. This trend was evident for levels of organic N, exchangeable cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+} and Al), exchangeable NO_3^{-} and total organic N (Table 6-1). Only exchangeable sulfate and exchangeable NH_4^{+} did not decrease with soil depth. Mean soil pH, on the other hand, increased with soil depth and was 3.75, 4.08 and 4.18 for the A, Bw and Cb horizons, respectively (Fig. 6-1).

Because the effective cation exchange capacity (CEC_e) was determined by the summation method, it showed the same decreasing trend with soil depth as the exchangeable cations, with means of 7.87, 4.98 and 3.52 $cmol_c\ kg^{-1}$ for the A, Bw and Cb horizons (Fig. 6-1). Exchangeable Al and H^{+} dominated the cation exchange complex of NDW soils with the base saturation being

Table 6-1. Mean concentrations and standard deviations of soil chemical parameters measured from A, Bw and Cb soil horizons in the NDW. Units are expressed in μeq kg^{-1} soil (n = 48) except total organic nitrogen in % weight.

Compositions	A		Bw		Cb	
	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation
Exchangeable SO_4	235	105	221	108	203	73
Total SO_4	858	356	1,187	625	1,887	1,086
Exchangeable NO_3	550	188	391	210	168	107
Exchangeable NH_4	57	67	89	70	92	94
Total Organic Nitrogen	0.43%	0.15%	0.23%	0.08%	0.14%	0.05%
Exchangeable Ca	1,183	945	550	191	528	568
Exchangeable Mg	478	271	255	44	171	75
Exchangeable Na	255	115	191	87	195	102
Exchangeable K	989	231	610	138	491	173
Total Exchangeable Base	2,905	1,328	1,606	254	1,386	735
Exchangeable Al	38,482	8,965	28,987	5,900	22,597	6,580

equal to or less than 4% of the total CEC_e, a severe level for soil sensitivity to acid deposition. Exchangeable H^+ content was over 36% of the CEC_e implying the importance of organic acids. The mean Ca/Al ratio for exchangeable phases was below 0.001 indicating a potential to impair plant growth.

Exchangeable Al concentrations decreased from 38,482 μeq kg^{-1} to 28,987 μeq kg^{-1} between the A and Bw horizons and reached a low of 22,597 μeq kg^{-1} in the Cb horizon (Table 6-1). The ratio of exchangeable base to exchangeable Al was less than 10 for all three soil horizons. Exchangeable Ca^{2+} and K^+ accounted for over 70% of the total exchangeable bases, which had mean values of 2,905, 1,606 and 1,386 μeq kg^{-1} in the A, Bw and Cb horizons respectively. The A horizon was higher in total exchangeable bases than the two lower horizons as the mean concentration was almost two times of those in Bw and Cb horizons.

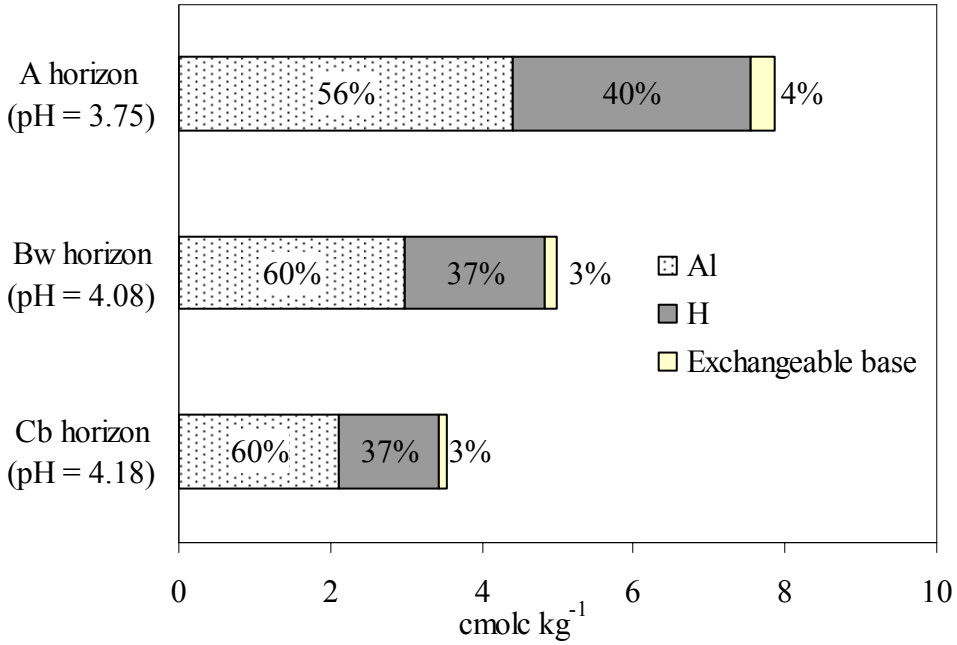

Fig. 6-1. Percent of the effective cation exchange capacity (CEC_e) comprised of basic and acidic cations for the different soil horizons. Values represent the mean of all sample sites (NS1-NS4) and sampling times.

Exchangeable sulfate was defined as the sulfate adsorbed by outer-sphere sorption and easily displaced by other anions. Total sulfate was taken as the sum of exchangeable sulfate and inner-sphere adsorbed sulfate, which is thought to be only displaced by high affinity anions. Soil content of exchangeable sulfate in the NDW was relatively uniform among A, Bw and Cb horizons, with mean values between 203 to 235 μeq kg^{-1} (Table 6-1). Total sulfate content increased with soil depth with means of 858 μeq kg^{-1} in the A horizon, 1,187 μeq kg^{-1} in the Bw horizon and 1,887 μeq kg^{-1} in the Cb horizon. In soil, over 50% of total sulfate was adsorbed by inner-sphere adsorption since the soil content of total sulfate was much greater than the amount of exchangeable sulfate.

Soil N is composed of organic N and inorganic N (NH_4^+, NO_3^-). The NO_3^- content in NDW was twice as high as the SO_4^{2-} concentration in the A horizon, but decreased significantly with

depth, becoming lower than SO_4^{2-} in the Cb horizon (Table 6-1). Mean nitrate contents in the A, Bw and Cb horizons were 550, 391 and 168 μeq kg^{-1} respectively. Soil NH_4^+ content was less than 100 μeq kg^{-1} in all soil horizons, with mean values of 57, 89 and 92 μeq kg^{-1} for the A, Bw and Cb horizons. Mean values of total organic N were approximately 1000 times greater than the combined levels of NO_3^- and NH_4^+. As with nitrate, mean organic N content decreased greatly with depth, being 0.43%, 0.23%, 0.14% from shallow to deeper soil horizons.

Sulfate Adsorption

In the sulfate concentration range used (0 – 400 μeq L^{-1}), adsorption saturation was not reached at the studied pH levels (4.0, 4.4, 5.0) (Fig. 6-2). This range in concentrations of sulfate solution was chosen because the maximum sulfate concentration recorded for soil water in the NDW was 350 μeq L^{-1}. Sulfate sorption in NDW soils (Inceptisols) was best approximated by the Freundlich equation rather than the Langmuir model, a result that was also found by Bolan et al. (1986). At high solution concentration, the maximum sulfate adsorption attained in the A horizon was approximately 1,400 μeq kg^{-1}, which was at least 200 μeq kg^{-1} lower than the maximum sorption attained in the Bw and Cb horizons, indicating a greater capacity to adsorb sulfate in lower soil horizons. At pH 5.0, the soil adsorption of sulfate was significantly lower than at pH 4.0 and 4.4 for the A and Cb horizons indicating the pH dependence of sulfate sorption. The experiment to investigate the relationship between sulfate desorption and pH indicated that the amount of desorbed sulfate increased linearly when soil pH increased from 4.3 to 5.5 (Fig. 6-3).

In the range of initial sulfate solution concentrations used in this study (0 – 400 μeq L^{-1}), desorption of sulfate was observed when initial sulfate concentration in solution was below 50 μeq L^{-1}. The change point from desorption to adsorption occurred when solution sulfate

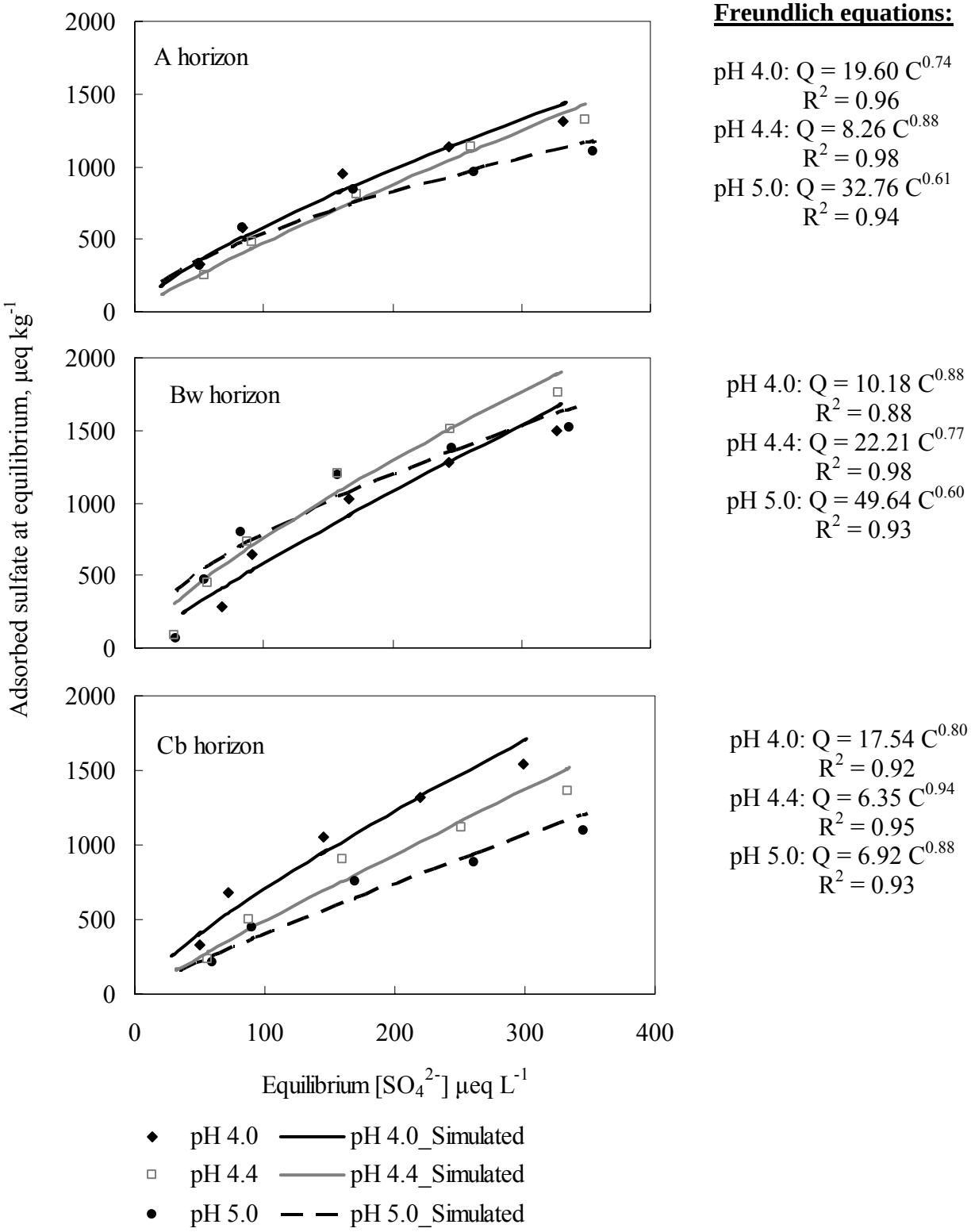

Fig. 6-2. Sulfate adsorption isotherms performed at pH 4.0, 4.4 and 5.0 on soil from the A, Bw and Cb horizons taken from the NS4 sample site in August of 2008. Lines and equations represent the fit of the Freundlich model.

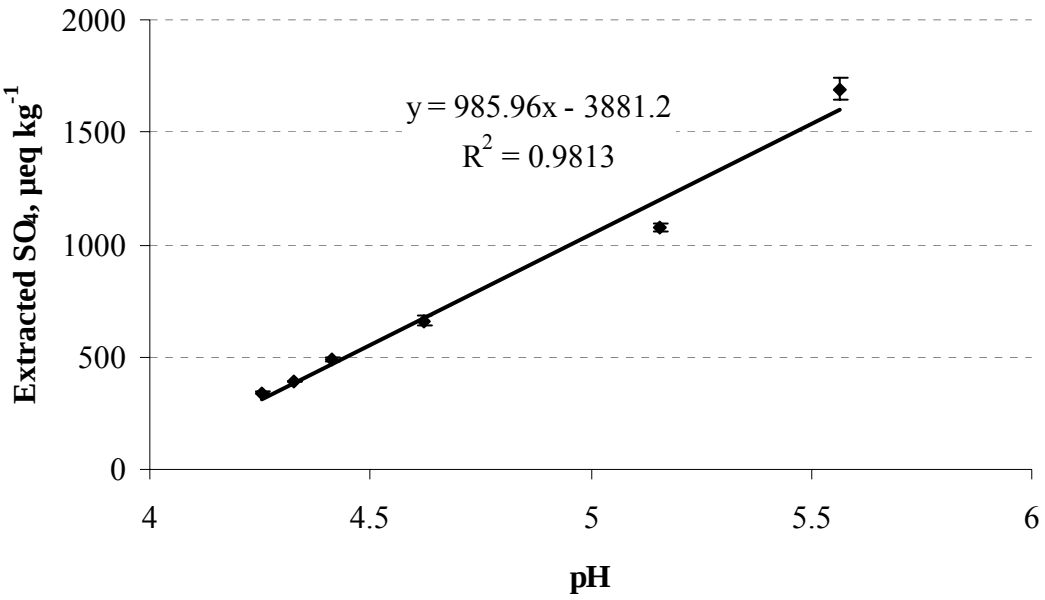

Fig. 6-3. Effect of pH on sulfate desorption from Bw horizon soil taken from the NS4 sample site.

concentrations were increased to around 50 µeq L^{-1}. These results suggest that sulfate will desorb from soils in the NDW when sulfate concentrations in soil solution are low and soil pH is higher, while the soil will adsorb sulfate from soil solution at higher concentrations and when soil pH is lower.

Nitrogen Mineralization and Nitrification

Because the presence of soil NO_2^- was insignificant, net mineralization rate was expressed as the change in total inorganic N (NO_3^- + NH_4^+) over the incubation period and nitrification was expressed as the change in NO_3^- over time. The slopes in the linear-fitted lines represent the mean net mineralization and nitrification rates over the 28-day incubation (Fig. 6-4). Both the net mineralization and nitrification rate showed a decreasing trend with soil depth, which parallels trends in organic N content (Table 6-1). Organic N was between 350 and 500 times greater than inorganic N content indicating a large sink for N and evidence for a biological control of N behavior in the NDW.

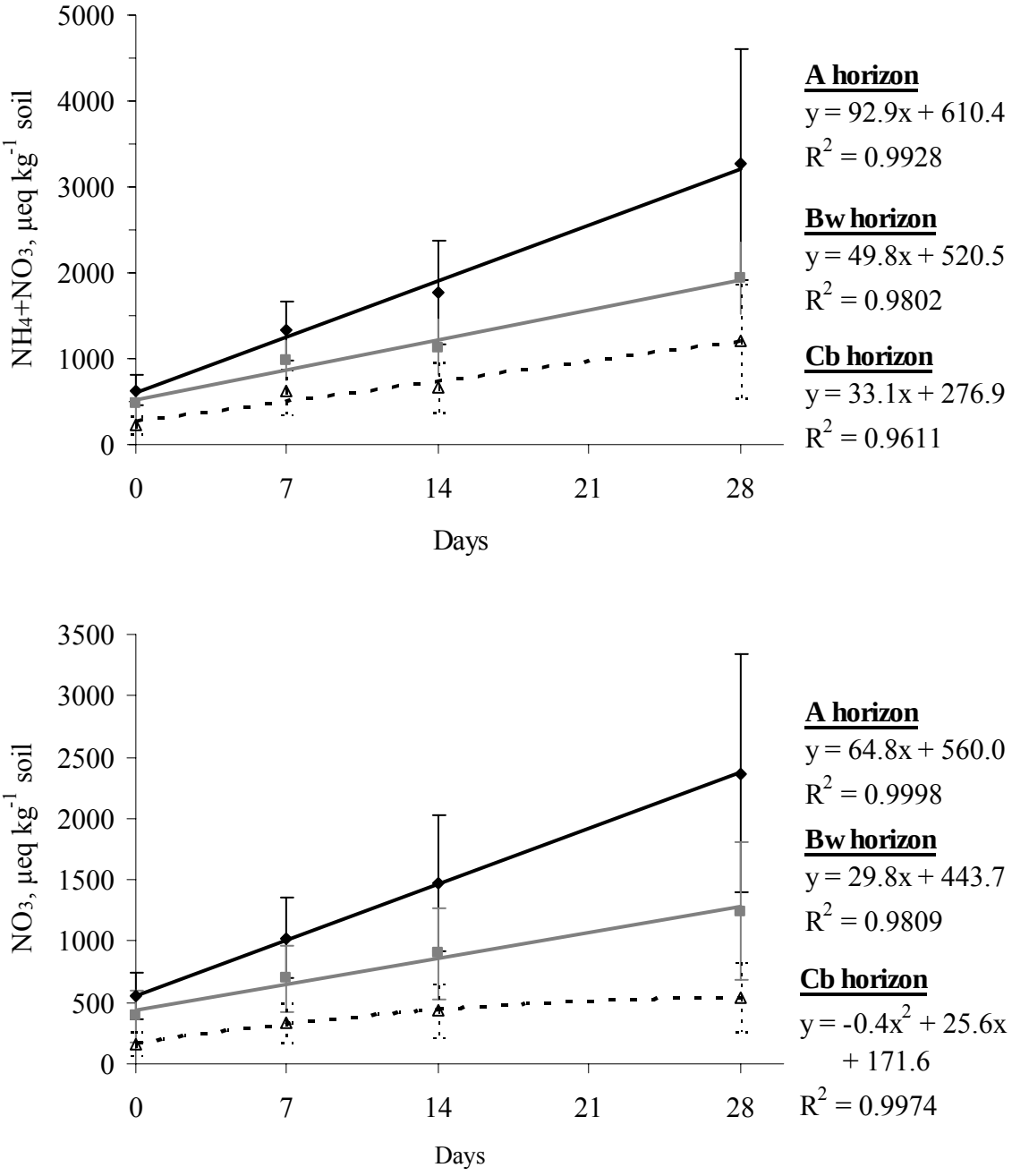

Fig. 6-4. Mean increase of NH_4^+ and NO_3^- content in soil over 7-, 14-, and 28-day laboratory incubation periods for A, Bw and Cb soil horizons. Values represent means of all sample sites and sampling times.

An initial flush of N mineralization occurred in all soil horizons during the first 7 days of incubation likely due to exposure to warm temperatures (~22°C). This early growth was followed by a slight decrease in the rate of mineralization during the second week, being more pronounced in the Bw and Cb horizons. During days 14-28 of the incubations, a small rejuvenation in mineralization rates is seen, perhaps indicating a new source of C from the death of heterotrophic microorganisms. Overall, a large degree of variability is seen in these results making it difficult to draw conclusions. During the second week of incubation some samples from the Bw and Cb horizons showed net immobilization suggesting decreased available N resources, although the median values were still positive (Fig. 6-5). It is clear, however, that mineralization in the A horizon, which contained a greater amount of total N, did not experience substrate limitation throughout the 28-day incubation.

Nitrification was greatest in the A horizon and remained constant throughout the 28-day incubation period, while the production of nitrate declined over time in the Bw and Cb horizons (Fig. 6-5). This indicates that either the growth of nitrifying bacteria was limited by NH_4^+ production or that heterotrophic microorganisms were immobilizing some of the nitrate produced by nitrifiers. The results also suggest that the nitrification potential of A horizon soil is not substrate-limited and is quite high, being approximately 66-90% of net mineralization. Sufficient organic substrate exists in this soil horizon to avoid competition for inorganic N between nitrifying autotrophs and heterotrophic soil microbes. Given suitable temperature and moisture conditions, the potential exists for relatively large amounts of nitrate to be produced in surface soils of the NDW which can potentially increase nitrate export from the watershed.

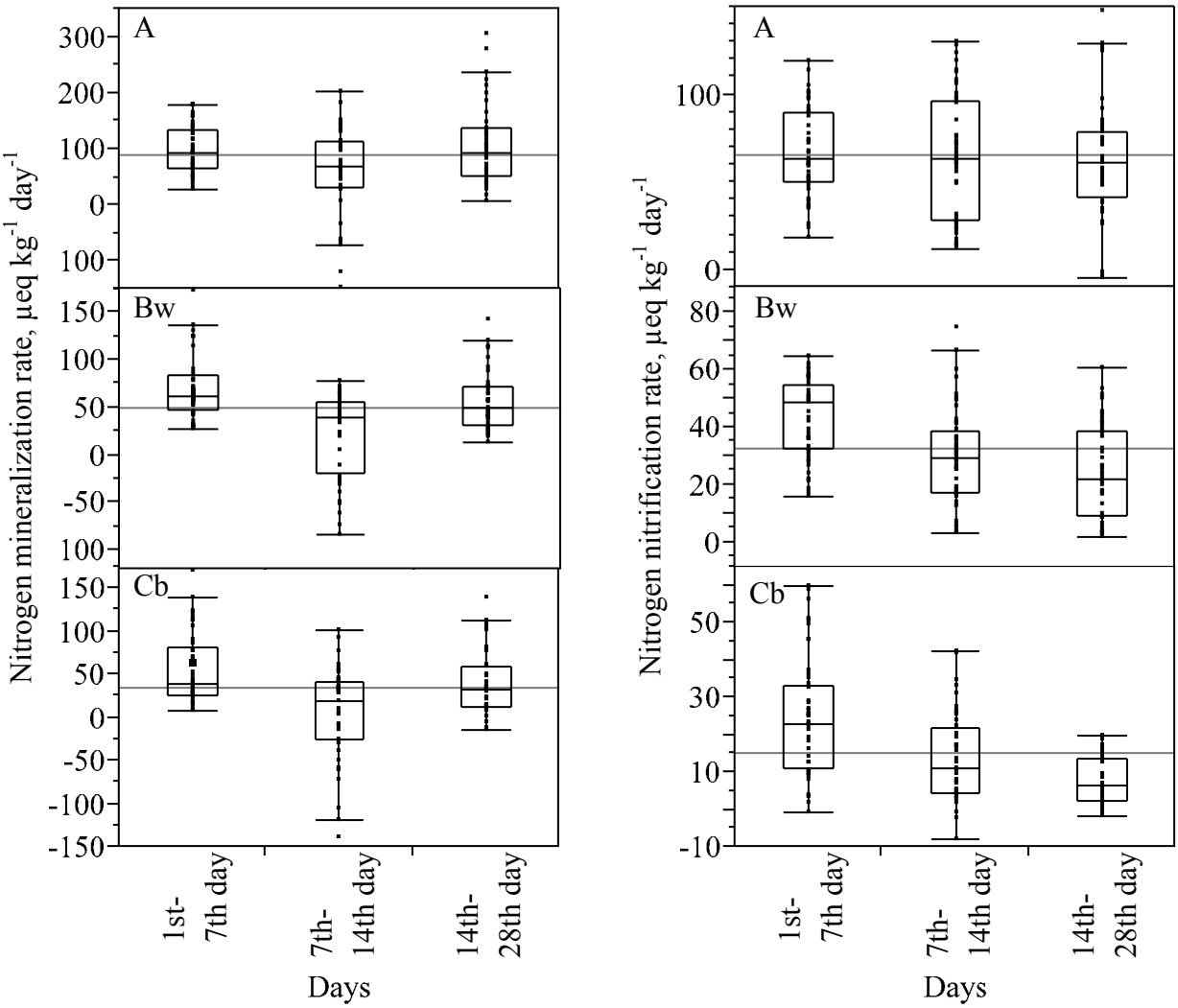

Fig. 6-5. Box plot of mineralization and nitrification rates for A, Bw and Cb soil horizons. Values represent means of all sample sites and sampling times.

DISCUSSION

Acid-base chemistry in the NDW was strongly affected by soil depth, but weakly by season and elevation. Organic nitrogen was the only measured parameter to be affected by season and elevation being lower under conditions more likely to promote mineralization, namely lower elevations and warmer seasons. The surface soil horizon had significantly higher concentrations of organic and inorganic N, base cations and aluminum and a greater CEC than deeper soil horizons. Significant differences among soil horizons illustrated the great variability in soil characteristics with depth and emphasized the need to sample soil horizons separately in order to fully describe the effects of acid deposition on watersheds.

Base cations made up only 4% of the soil CEC_e, with the vast majority of negative exchange sites being occupied by aluminum and H^+. A soil is defined as being acid-sensitive if the base saturation is below 10% (Helliwell et al., 1998; Tao et al., 2002; Sullivan et al., 2006). Although the depletion of base cations is a natural process in soils of the humid southeast, acid deposition undoubtedly contributed greatly to the low base saturation in these soils. The depletion of soil base cations has been shown to delay ecosystem recovery from acidification (Malek et al., 2005). Along with the depletion of base cations, the extremely low Ca/Al ratio of < 0.001 in the NDW is another sign of ecosystem degradation from long-term acid inputs. The ratio of Ca/Al has been used as an indicator of the level of Al that can be toxic to plants (Cronan and Grigal, 1995). Low Ca/Al ratios have been shown to have adverse impacts on tree growth and nutrient supply, and may result in a decline in forest productivity and dieback (Lawrence et al., 1995).

As plant uptake and leaching of sulfate is insignificant, soil sorption/desorption is the main driver of sulfate behavior (Garten et al., 1988; Lindberg and Garten, 1988; Lindberg and Lovett,

1992). The adsorption and desorption processes are particularly important in soils with high sulfate sorption capacity and receiving high levels of sulfate deposition (Alewell, 2001). The NDW has received high rates of acid deposition, but continues to behave as an overall sink for sulfate. This was demonstrated by the results of sulfate adsorption isotherms showing that the adsorption capacity of soils in the NDW is not currently saturated. In a recent study, the NDW was found to retain 61% of sulfate entering the watershed based on an input-out budget. Combined with our results this suggests that the majority of sulfate deposition in the NDW is not being exported to streams due to adsorption to soil. Without this retention of sulfate, acidity in streams draining the NDW would likely be even greater than current levels.

The retention of sulfate in acid-impacted watersheds has the potential to delay recovery from the effects of acid deposition (Kahl et al., 2004; Sullivan et al., 2008). At low sulfate concentrations in soil solution, adsorbed sulfate may desorb, resulting in further reductions in stream ANC and pH. It has been suggested that soils in the southeastern Appalachian region have not yet fully realized the effects of acid deposition because of watershed retention of sulfate (Herlihy et al., 1993; Sullivan et al., 2008). Under future scenarios of reduced sulfate deposition, the release of this previously bound sulfate can be expected (Blake et al., 1999). Based on our results, a reduction of sulfate in soil solution caused by a decrease in deposition may lead to the release of sulfate from soils in the NDW. Below sulfate concentrations of 50 $\mu eq\ L^{-1}$, soils of the NDW will be expected to lose sulfate through desorption of previously adsorbed sulfate. However, it is important to note that the Freundlich model used assumes that sulfate adsorption to soil is fully reversible, yet it is known that sulfate sorption is at least partially irreversible (Gobran et al., 1998). Therefore, desorption of sulfate cannot be fully predicted by the

Freundlich model, and our results may overestimate the potential for desorption of sulfate in the NDW.

Adsorption and desorption of sulfate from soil is related to soil solution pH (Sokolova and Alekseeva, 2008) and organic C and their interactions. Our finding of lower sulfate adsorption at higher pH was consistent with many other studies that have found that minerals with positive surface charge were capable of adsorbing more anions at lower pH values (Nodvin et al., 1986; Martinez et al., 1998; Martinson and Alveteg, 2004). Besides pH, sulfate adsorption is known to also be affected by organic C. Pigna and Violante (2003) found that organic C strongly inhibited the adsorption of sulfate in the surface horizon of Inceptisols although this effect was dependent on soil pH (Gobran et al., 1998). The lower capacity for sulfate adsorption found in the A horizon of the NDW relative to the Bw and Cb horizons was probably due to the higher organic C content in the A horizon. Analysis of soil from the NDW in the 1990s found that the soil organic C content in the A horizon was at least two times greater than that measured in the B horizon (Ammons, unpublished data).

The high level of organic N present in NDW soils suggests that the internal cycling of N is an important driver in regulating levels of nitrate export from the watershed (Johnson and Lindberg, 1992). Therefore, determining the mineralization and nitrification rates could be a useful tool to predicted nitrate loss. Net mineralization and nitrification rates have been reported to be 156-236 $\mu eq\ kg^{-1}\ day^{-1}$ for mineralization, and 15-45 $\mu eq\ kg^{-1}\ day^{-1}$ for nitrification processes in other watersheds (Koopmans et al., 1995; Jefts et al., 2004). Our results for net mineralization and nitrification rates were in the same order as these studies. In addition, the declining trend of N transformation rates with increasing soil depth were in agreement with many other findings, where uppermost soil layers were found to account for most of the inorganic N supply (Persson

and Wirén, 1995). The high rates of N transformation imply that watershed nitrate is biologically driven rather than controlled by nitrate deposition (Koopmans et al., 1995; van Miegroet et al., 2001) meaning that a reduction of N deposition in the watershed might not directly affect N loss. Watershed characteristics affecting biological activity, such as forest type, elevation, organic nitrogen content and C:N ratio would be more important in determining stream N concentrations.

Net nitrification/net mineralization rates were between approximately 66-90% for the A soil horizon which is within the range found by others in southeastern forests (Joslin et al., 1992; Williard et al., 1997). The net nitrification/net mineralization ratio in the Bw and Cb soil horizons was lower than for the A horizon but were still relatively high, ranging from ~43% to 78%. Williard et al. (1997) suggest that high net nitrification/net mineralization ratios indicate that N is not limiting microbial activity and nitrifiers are producing more nitrate than can be immobilized. This finding is consistent with high nitrate exports to streams suggests N-saturation. The NDW has been reported to be in Stage 2 N-saturation (Nodvin et al., 1995; van Miegroet et al., 2001) which is characterized by high nitrification and elevated nitrate concentrations in streams. Stage 3 N-saturation is indicated when N outputs exceed inputs (Fenn et al., 1998). The NDW appears to be retaining nitrate to some degree despite the nitrate export to streams and, therefore, is most likely still in Stage 2. It should be noted that net mineralization and nitrification were measured at room temperature (~ 22^{o}C), which was higher than field temperature for most seasons. In addition, homogenized soils were used in the laboratory incubations. Therefore, the mineralization and nitrification rates determined in the laboratory incubations are expected to be greater than rates that would be found in the field. Jefts et al. (2004) reported that the difference in magnitude between laboratory and field rates of

mineralization and nitrification could be one to four times. Measurement of *in situ* rates of mineralization and nitrification is a next step for further study.

CONCLUSIONS

Chemical composition of soil in the NDW is dominated by organic N, organic C and Al. Mean base saturation was below 4% of the CEC_e , indicating that this watershed is very sensitive to acid deposition. In all three soil horizons, calcium and potassium dominated the base cations. However, the ratio of Ca/Al was below 0.001. This especially low ratio implied that the forest growth may be negatively affected due to deficiency of nutrients and the toxicity of Al. Adsorption isotherms of sulfate fit the Freundlich model and suggest that these soils have not reached their maximum adsorption capacity. Therefore, the NDW is currently behaving as a sink for sulfate. However, sulfate desorption may be expected at low sulfate deposition or high pH. Nitrogen cycling was controlled by biological transformations rather than atmospheric deposition. Because of the especially high organic N content, the watershed had a high potential for mineralization and nitrification especially in surface soil. This research provides essential information on the acid-base chemistry of the soils in the NDW, a key component for understanding the potential for ecosystem recovery. The continued export of both sulfate and nitrate from the watershed despite decreases in deposition can potentially delay watershed recovery. This data can help improve watershed models to better predict the response of high elevation watersheds in the southeastern US to future changes in acid deposition.

CHAPTER 7 RESPONSE OF SOIL WATER CHEMISTRY TO SIMULATED CHANGES IN ACID DEPOSITION IN THE GREAT SMOKY MOUNTAINS

ABSTRACT

Long-term acid deposition in the Noland Divide Watershed (NDW), a high-elevation watershed in the Great Smoky Mountains National Park, led to the soil base saturation to below 5%. With such low buffer capacity, the watershed recovery in response to future reduced acid loads is difficult to predict. A laboratory column leaching experiment and field lysimeter experiment were designed to investigate the soil response to reduced deposition loads of sulfate and nitrogen. Soil columns were leached for 92 days with synthesized solutions which simulated five acid deposition scenarios including the current acid deposition load. The future reduction scenarios were: 50% reduction of SO_4^{2-} and 48% reduction of NO_3^- as well as 9% increase of NH_4^+; 90% reduction of SO_4^{2-} and NO_3^- and 40% reduction of NH_4^+; 90% decrease of SO_4^{2-} and NO_3^- and 80% decrease of NH_4^+; 61% reduction of SO_4^{2-} and 26% reduction of NO_3^- as well as 94% reduction of NH_4^+ (stream water from the NDW). Additionally, a 30-m^2 field site was covered and irrigated with NDW stream water instead of rainfall to study the soil drainage chemistry in an ambient environment in the summer of 2008. With current levels of soil acidity, the neutralization of protons added by deposition or internal nitrification reactions was dominated by mineral weathering, dissolution of Al^{3+}, cation exchange of base cations and SO_4^{2-} adsorption reactions. Data from this study suggest that current soil pools of Ca^{2+} and Mg^{2+} will be fully depleted in the next 45 to 70 years. Along with the continued reduction of those cations, depletion of K^+, Mn^{2+} and Zn^{2+} should become more important in the future. Based on evidence from this study watershed recovery from acidification in the NDW, evidenced by retention of base cations, will start only when deposition loads of sulfate are reduced by more than 60% from current levels. An increase in deposition pH from 4.4 to 6.1 also improved retention of base cations. Sulfate was retained in soil through adsorption at current deposition load but was

desorbed from soil when deposition load of sulfate was reduced by 60%. Protons released by sulfate desorption via ligand exchange elevated the depletion rates of base cations and delayed watershed recovery. Besides the important effect of deposition loads, water throughflow rate in soil had a significant effect in controlling soil drainage chemistry and time trends. Short travel time during fast throughflow minimized the time-related reactions, such as adsorption/desorption of SO_4^{2-}, nitrification, and mineral weathering in this study. In contrast, slow throughflow increased reaction time and caused greater variability of effluent chemistry. Dissolution of Al appeared to be instantaneous and was controlled by pH rather than throughflow rate. The column leaching and field lysimeters experiments provide some important information to predict watershed recovery in response to future reduced acid deposition loads.

Key Words: acid rain, acids, cations, chemical properties, flow rate, leaching, soil analysis, soil water

INTRODUCTION

Biogeochemical processes in soil contribute greatly to the effect acid deposition has on stream water quality in a given watershed. Soil processes are found to play an important role in neutralizing added acidic ions by releasing base cations, hydrolyzing aluminum, and adsorbing sulfate (Nilsson and Tyler, 1995; Driscoll et al., 2001; Jönsson et al., 2003). A few studies have also found that acidification can affect heavy metals in soil by dissolving into solution at relatively low concentration levels (Szillery et al., 2006; Stevens et al., 2009). The Noland Divide Watershed (NDW), a high-elevation watershed in the Great Smoky Mountains National

Park (GRSM), is particularly vulnerable to acid deposition due to its low base cation pool; soil base saturation is below 5% and the exchangeable Ca:Al mole ratio is 0.001 (Chapter 6). Although surface water draining from the NDW is acidic (pH<6.0 and ANC<20 μeq L^{-1}) which has caused high levels of aluminum and nitrate in streams, sulfate levels are moderately low despite high deposition. This is because the watershed is retaining signification amounts of added sulfate (61% of throughfall sulfate) via soil adsorption. Based on data from adsorption isotherms, the soils of the NDW have not yet reached a sorption maximum, meaning they have an ability to sorb further inputs of sulfate. The behavior of retained sulfate with reductions in sulfate deposition, on the other hand, is more difficult to predict. Yet future deposition loads are forecasted to be much lower than current levels. A major concern in this case, is the potential rapid desorption of retained sulfate from soil and the subsequent effects this may have on other watershed processes.

Efforts by a number of countries to control acid deposition have focused on cutting emissions of sulfur dioxide and nitrogen oxides from industry. The United States government has passed the Clean Air Act (CAA) of 1970 and the CAA Amendments of 1990 with the overall goal of achieving significant reductions in emissions of sulfur dioxide and nitrogen (N) oxides (USEPA, 1970, 1990). Since the implementation of the Clean Air Act and the 1990 amendments, SO_2 emissions from electric utilities have decreased by 24% from 1970 to 1998 in the U.S. (Shannon, 1999; Driscoll et al., 2001). However, the emission of NOx has remained fairly constant since 1990 (Fernandez and Wortman, 1997; Stoddard et al., 2003). It therefore becomes especially important to be able to predict the response of forested watersheds and streams to decreases in acid inputs.

Although soil acid neutralization processes have been conceptually studied by many, it is difficult to predict watershed recovery behavior from models (Clayton et al., 1991b). By measuring changes in soil solution chemistry, watershed responses to changes in atmospheric inputs can be determined. Because soil solution reacts quickly to changes in conditions either chemical or physical, studying its change is an efficient way to predict soil responses to changes in acid deposition. Therefore, soil leaching experiments are often conducted in laboratory columns or in the field to predict watershed response to changes in input loads (Persson and Wirén, 1995; Hodson and Langan, 1999; Lamersdorf and Borken, 2004). In this way, inputs can be controlled to mimic future levels of deposition (Clayton et al., 1991b; Calace et al., 2001; Dubiková et al., 2002). Studies in the European Union (EU) have simulated depositional changes in N and sulfate (Bredemeier et al., 1995; Beier et al., 1998; Bredemeier et al., 1998; Wright and Rasmussen, 1998). These studies found that reductions in sulfate and N inputs led to decreased concentrations of these chemicals in soil solution but that the recovery of acidification was slow and minimal. Other studies, mostly in North America, have focused on watershed response to artificially elevated levels of N and sulfate (Currie et al., 1999; Edwards et al., 2002; Fernandez et al., 2003; Evans et al., 2008). These enrichment experiments concluded that the increased acid input enhanced the depletion of soil base cations. It is important to investigate the effect of reduced deposition of both N and S together to predict future watershed recovery from acidification. To our knowledge, no field experiment in North America has been conducted to study soil drainage chemistry in response to reduced acid deposition loads of both N and sulfate, especially in an extremely acidified watershed like the NDW.

The objective of this study was to investigate soil responses of soil drainage chemistry to reduced acid deposition based on two experiments: 1) a laboratory column experiment in which

homogenized soil from the NDW was exposed to simulated acid deposition at five different deposition scenarios; and 2) a field experiment in which in situ lysimeters were used to collect soil leachate from a 30-m^2 site within the NDW which received irrigated stream water. The aim of both experiments was to simulate reduced deposition scenarios and examine the effect on soil drainage chemistry. The experimental results can be used to predict the future watershed response to reduced acid deposition.

METHODS

Soil Column Leaching Experiment

In July of 2008, soil samples were taken using a cylindrical auger from the A, Bw and Cb horizons at the soil leaching experiment site as shown in Fig. 1. Samples were air-dried and passed through a 2-mm sieve to be used for chemical analysis and for the column leaching experiment. The exchangeable anions, base cations and the change in inorganic N and sulfate during a 28-day incubation experiment were analyzed by the methods described in Chapter 6. Briefly, exchangeable SO_4^{2-}, NO_3^- and NH_4^+ were extracted by 50 ml of 0.5 mM KCl with 5 g soil and measured by Dionex ion chromatography (IC). Exchangeable base cations were determined by extraction of 5 g soil in 50 ml 0.2M NH_4Cl and analyzed by inductively coupled plasma spectrometry (ICP). Soil samples were incubated at 22^oC for 28 days to determine the change in inorganic N and SO_4^{2-} levels due to biological reactions. These chemical properties are shown in Table 7-1.

For the column leaching experiment dried and sieved soil from each soil horizon was packed into glass cylinders (inner diameter=60 cm; length=47 cm). The bottom of each column was sealed except for a 1-cm opening from which effluent was collected. Soil from the different

Table 7-1. Properties of NDW soils used for laboratory column leaching study.

	A horizon	Bw horizon	Cb horizon
Wet soil weight, g	100	390	500
Moisture, %	37.85	32.43	24.76
Packed soil length in column, cm	4	14	18
Organic nitrogen, %	0.35%	0.30%	0.14%
Chemical composition, μmol kg^{-1}			
Exchangeable NH_4^+	512	217	165
Exchangeable NO_3^-	1,287	535	349
Exchangeable SO_4^{2-}	179	272	167
Exchangeable Na^+	363	414	299
Exchangeable K^+	1,386	1,030	751
Exchangeable Mg^{2+}	323	220	125
Exchangeable Ca^{2+}	671	536	303
Change rate of nitrogen during 28-day laboratory incubation			
Nitrogen mineralization rate, μmol kg^{-1} day^{-1}	92.9	49.8	33.1
Nitrification rate, μmol kg^{-1} day^{-1}	64.8	29.8	11.3
Change rate of sulfate during 7-day laboratory incubation			
Sulfate change rate, μmol kg^{-1} day^{-1}	-7.5	-6.3	-5.6

horizons was sequentially packed into each column to the following depths: A=4 cm; Bw=14 cm; Cb=18 cm with horizons being separated by nylon mesh (Fig. 8-1). The soil horizon depths used in the columns were equivalent to half of the field horizon depth. The packed soil columns were kept in a room at constant temperature (22^{o}C) and wrapped on the outside with aluminum foil to provide a dark environment for the soil.

Four deposition scenarios were used to simulate the current level and potential future levels of SO_4^{2-} and N (NO_3^- and NH_4^+). A fifth artificial deposition treatment was included consisting of stream water from the NDW.

Scenario 1 – Current deposition in NDW based on mean volume-weighted throughfall concentrations collected between1991 and 2006 (Chapter 3);

Scenario 2 – 50% SO_4^{2-} reduction, 48% NO_3^- reduction, 9% NH_4^+ increase;

Scenario 3 – 90% SO_4^{2-}reduction, 40% NO_3^- reduction, and 40% NH_4^+ reduction;

Scenario 4 – 90% SO_4^{2-} reduction, 90% NO_3^- reduction, 80% NH_4^+ reduction;

Scenario 5 – NDW stream water from the SW stream which represents a 61% SO_4^{2-} reduction, 26% NO_3^- reduction, 94% NH_4^+ reduction.

The percent change from current deposition amounts depicted in Scenario 2 represents the predicted 2018 levels of SO_4^{2-}, NO_3^- and NH_4^+ based on CMAQ model simulations (GRSM Park staff, personal communication). Scenario 4 corresponds to the percent reductions in NO_3^- and NH_4^+ required to achieve a total N deposition target in the NDW of 5 kg ha^{-1} yr^{-1}, also based on the CMAQ model. The percent changes in Scenario 3 are purely hypothetical.

Artificial deposition solutions were prepared containing the appropriate concentrations of SO_4^{2-}, NO_3^- and NH_4^+ for each scenario. It was assumed that the amounts of Ca^{2+}, Mg^{2+} and K^+ in future deposition scenarios will not change from current amounts. Solution pH was maintained

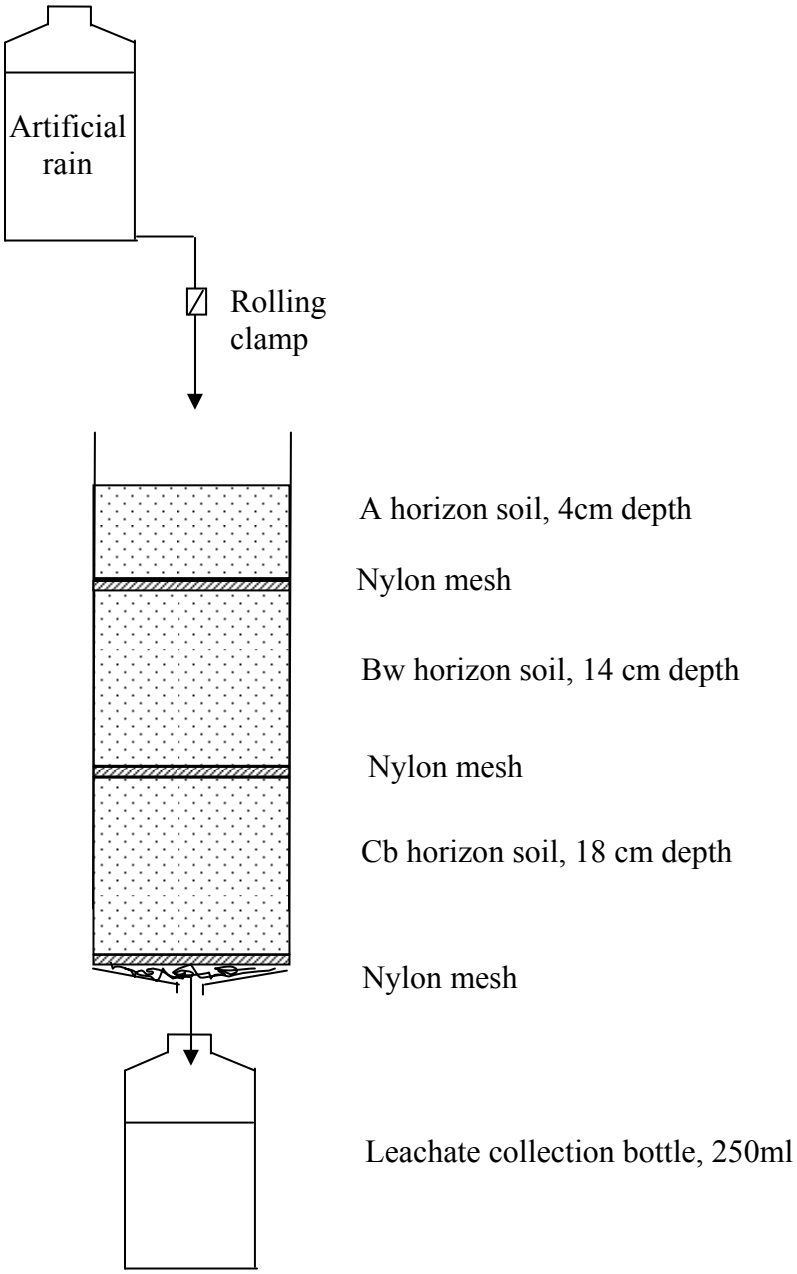

Fig. 7-1. Schematic illustration of soil leaching column experiment setup. The specification for the glass column was: external diameter = 64 mm, inner diameter = 60 mm, length = 45 cm; the outside wall of the column was covered with aluminum.

at 4.7, which is the average wet deposition pH for the NDW (Chapter 3). Prepared inflow solutions for each deposition scenario were applied to the top of triplicate soil columns at a constant flow rate of 1.77 mm hr^{-1}. This flow rate was designed to be similar to the average precipitation rate, 2.16 mm hr^{-1}, recorded at a weather station close to the NDW. After 1000 ml of solution were applied to each column, application of inflow solution was discontinued for 1 to 3 days, followed by the addition of another 1000 ml of artificial deposition solution in order to simulate natural wetting and drying periods. The soil column experiment was conducted for 92 days in 2008 until effluent concentrations of most chemicals reached steady state. The total solution added to each column was approximately 150 cm. This amount of solution was approximately two-thirds of the actual annual throughfall deposition recorded for the NDW. 2009). Effluent from each column, collected in 250 ml increments, was filtered through a 0.4-μm membrane filter and analyzed for pH, acid neutralizing capacity (ANC), conductivity by an Mantech Autotitrator, anions (Cl^-, SO_4^{2-}, NO_3^-) and ammonium by a Dionex IC 2500, and base cations and dissolved metals (Al, Cu, Fe, Mn, Si, Zn) by ICP.

Calculation of Proton Budget

Proton balances to identify acid inputs, outputs and buffering mechanisms in soil can aid in the understanding of watershed acidification processes. To investigate the contribution of various soil chemical processes in regulating the acid/base chemistry in the soil columns, the mass of protons released or neutralized by each reaction was calculated according to the equilibrium reaction. In this way the theoretical proton flux under each deposition scenario was calculated.

Proton sources. The measured pH in influent solution was used to calculate the influent H^+ flux. Nitrification produces two moles of proton and one mole of NO_3^- while consuming one mole of NH_4^+. Therefore, the proton produced by nitrification was estimated by doubling the

difference between influent and effluent NO_3^- concentrations. Desorption of SO_4^{2-} was another important proton source in the NDW which has been shown to contain a significant amount SO_4^{2-} by adsorption to soil.

*Proton sink*s. The amount of protons discharged in column effluent was calculated by using the measured effluent pH for each column. Reactions which consume protons included base cation/metal exchange, weathering reactions, Al dissolution and SO_4^{2-} adsorption reactions. It has been reported that the amount of dissolved silica in effluent can be used as an index of weathering (Dahlgren et al., 1990; Guicharnaud and Paton, 2006). The moles of protons consumed by the neutralizing reactions were estimated by the difference between influent and effluent concentrations of base cations and metals, dissolved Si, Al and SO_4^{2-}. The change in chemical concentrations inside the column was not considered in the proton budget as the total effluent solution collected was 10-fold greater than the column pore volume. Consequently, the calculation error due to ignoring the chemical concentration changes inside the columns was less than 10% and was excluded from the overall calculation.

Field Lysimeter Experiment

Because the laboratory column study involved using sieved, repacked soil, the columns do not accurately represent the heterogeneous nature of water flow, and thus solute flow, paths. Therefore, an in-situ lysimeter experiment was included to examine the comparability of laboratory results to field conditions. A 30 m^2 (5m × 6m) site within the NDW was selected in order to conduct the soil leaching experiment (Fig. 2-1). The entire site was covered with translucent 0.15-mm thick plastic sheeting at ground level to exclude rainfall from the study plot. A trench was dug on the upslope side of the site to prevent runoff from entering the study plot. An irrigation system was constructed underneath the plastic sheeting by connecting 2.54-

cmplastic piping with 1.57-mm holes drilled every 0.3 m. Stream water was conducted into the irrigation system at 30 m upstream of the SW stream weir and applied continuously to the study site at an average rate of 2.5 mm hr^{-1}. In this way, the SW stream water served as artificial deposition fitting a scenario of much lower acid input. The stream water has a much lower S and N load and a higher pH and ANC as compared with natural deposition in the NDW. Thus, this allowed us to examine how reductions in acid deposition will affect soil solution chemistry in the field. Current annual concentrations for deposition can be found in Chapter 3. Briefly, throughfall pH and ANC were measured as 4.3 and -24.5 respectively compared to 6.1 and 6.9 for SW stream water. Volume-weighted concentrations of SO_4^{2-} and NO_3^- were 60% and 30% lower in SW stream water while NH_4^+ was 95% lower.

Four V-shaped stainless steel pan lysimeters (surface area = 0.57 m^2) were installed 70 cm below the soil surface to collect soil leachate. Leachate from each lysimeter was collected in amber bottles and taken back to the University of Tennessee Water Quality Laboratory for chemical analysis weekly or biweekly. Solution samples were analyzed for anions (Cl^-, SO_4^{2-}, NO_3^-), cations (NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, K^+), pH, ANC and dissolved metals (Al, Cu, Fe, Mn, Si, Zn).

Southwest stream water was continuously irrigated on the experimental site from July 17 to Nov. 9, 2008. The total amount of water applied was 66.3 m^3 and the average water flow into the study area was 0.8mm hr^{-1}. Due to soil heterogeneity, the flow rate for each lysimeter varied. Lysimeters can have a collection efficiency of less than 10% due to water divergence (Jemison and Fox, 1992; Zhu et al., 2002). In our study, the average collection efficiency was estimated to be less than 15% by calculating the average ratio of leachate water collected to the total amount of water irrigated on the 30-m^2 site.

Data Analysis

Volume-weighted concentrations of solution from both the column and field experiments were used to evaluate the significance of changes in chemical constituents at the different simulated deposition load scenarios. Statistical analysis of trends in chemical concentration over time was preformed with Origin 7.5. A significant time trend for all data was identified by a *p*-value less than 0.05.

RESULTS AND DISCUSSION

Soil Column Study

The effect of the different deposition scenarios on column effluent chemistry as a function of pore volume (PV) is shown in Fig. 7-2. Despite the different chemical composition of the influent solutions for the five deposition scenarios, the time trend of column effluent chemistry showed similar patterns. The effluent pH in all scenarios decreased linearly from 4.7 to approximately 4.4 after 6 PVs of simulated acid rain passed through the columns. Most of the chemical constituents measured reached a steady state concentration after 2 PVs of influent solution was applied. The concentrations of NO_3^-, Ca^{2+}, Mg^{2+} and dissolved Al, Mn and Zn in effluent were best described by breakthrough curves, which showed a rapid decrease initially followed by attainment of steady state. In contrast, effluent concentrations of SO_4^{2-} showed an increasing trend during the first 2 PVs of influent addition and reached a maximum at steady state (Fig. 7-2). Even though there were no metals in any of the influent solutions, small amounts of dissolved Mn and Zn were released from soil columns. Trends in effluent concentrations of K^+ and dissolved Si over cumulative pore volumes did not follow that of other elements. Effluent

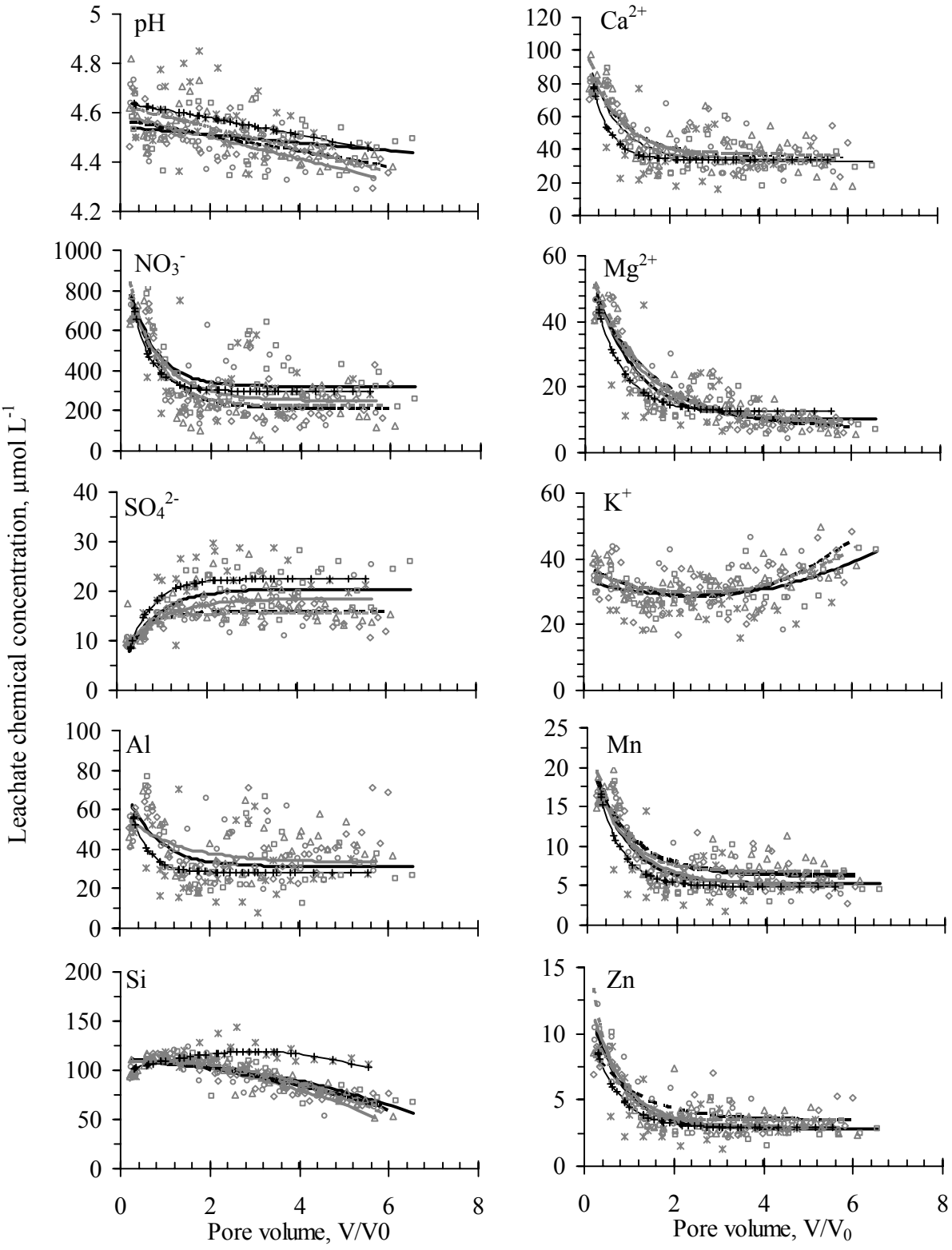

Fig. 7-2. Dissolved chemical composition of column effluent with increasing inflow depth under five simulated deposition scenarios: 1(□), 2(○), 3(◇), 4(△), 5(*). Lines represent best fit curves.

concentrations of NH_4^+ and dissolved Cu and Fe were extremely low and could not be fitted by any curve.

Comparison of influent and effluent concentrations was used to evaluate whether ions were retained in or depleted from the watershed in order to explore the possible reactions associated with watershed acidification or recovery. The volume-weighted mean effluent pH was 4.5 when the pH of the influent solution was 4.7 (scenarios 1-4), and 4.6 when influent pH was 6.1 (scenario 5) (Table 7-2). The similar effluent pH values from all columns despite the significantly different influent pHs implies that effluent pH was controlled by internal processes occurring in the soil column rather than the pH of the influent solution. The continued decreasing trend of pH over the course of the 92-day experiment despite the attainment of steady state by acidic anions suggests that the production of protons continued to occur with increased pore volumes, probably due to continued nitrification and/or sulfate desorption (Fig. 7-2). This result suggests that soils in the NDW have a low capacity to buffer changes in pH, at least under the conditions of our column experiment.

Acid Anions

Mean SO_4^{2-} concentrations in effluent from all artificial deposition scenarios were remarkably similar, 15-20 μmol L^{-1}, even though influent SO_4^{2-} concentrations varied from 4.9 to 56.8 μmol L^{-1} (Table 7-2). The level of sulfate in soil solution was controlled by adsorptive/desorptive processes in the column soil. Sulfate was retained in column soil at influent SO_4^{2-} concentrations above 25 μmol L^{-1}, but released when influent SO_4^{2-} concentrations fell below 15 μmol L^{-1}. This finding supports results from sulfate adsorption isotherms performed on NDW soils which showed that adsorption occurred when solution SO_4^{2} concentrations were 25 μmol L^{-1} or greater (Chapter 6). Therefore, under the current deposition load (scenario 1) sulfate is expected to

continue to be retained in the near future. Our hypothesis was that future reductions in sulfate load would cause a shift to sulfate desorption in this watershed, thus significantly delaying recovery from acidification. However, when the artificial sulfate deposition load was reduced by 50% (scenario 2), SO_4^{2-} was retained in soil columns. Only when sulfate in deposition was reduced by 60% or more of current amounts (scenarios 3-5) did SO_4^{2-} desorption occur.

Adsorption/desorption of sulfate affects soil drainage pH in the following way. During adsorption, SO_4^{2-} is exchanged for OH^- on positively charged ligand exchange sites, resulting in a proton being consumed from soil solution. In this way the adsorption of sulfate to soil is an important process for neutralizing protons (Martinson et al., 2003; Pigna and Violante, 2003). The opposite occurs upon sulfate desorption, with an OH^- taking the place of the desorbed sulfate anion on the ligand exchange site, thereby releasing H^+ into solution in order to maintain charge balance. Therefore, if a shift from sulfate adsorption to desorption occurs with future reductions in sulfate deposition, we can expect a delay in watershed recovery as protons are produced and base cations continue to be leached despite the reduction in sulfur deposition load (Stoddard et al., 1999). Due to the high buildup of previously adsorbed sulfate in NDW soils, this process could potentially continue for quite some time.

Nitrate exhibited significant mobilization in columns as the mean effluent NO_3^- concentration was approximately 300 μmol L^{-1} greater than the influent NO_3^- concentrations. The high concentration of effluent NO_3^- was partially due to the conversion of almost all the added NH_4^+ to NO_3^- via nitrification as evidenced by the low mean effluent NH_4^+ concentration (<2 μmol L^{-1}). However, mineralization of organic N contained in the soil must have also occurred as the levels of NH_4^+ added in column influent were relatively low and cannot account for the high level of nitrification occurring in the soil columns (Table 7-2). The level of organic N is high in

NDW soils (Chapter 6) and it is unlikely that most of this organic N would have been lost during air drying of the soils prior to repacking in the columns. Results from our soil column study indicate that soil nitrification was the main internal source of protons adding more than 93% of the calculated H^+ (Table 7-3). As the major process controlling the addition of protons, nitrification can contribute to the mobilization and release of base cations and metals (Berdén and Nilsson, 1996). This effect was evidenced by the positive correlation that exists between concentrations of NO_3^- and cations (Ca^{2+}, Mg^{2+}, Al^{3+}, Mn, and Zn) in the soil columns (data not shown). These results suggest that even with drastic reductions of depositional N, native sources of N production will continue to add NO_3^- to soil solution and produce acidity.

A number of caveats must, however, be taken into consideration when interpreting the above results. Soil columns were kept at a constant temperature of 22°C and were kept moist through a consistent flow of influent solution, with the exception of a 1-3 day drying period. The nitrification rate is expected to be much lower in the field as temperatures and moisture conditions would not be as favorable for the occurrence of nitrification. Soil disturbance caused by sieving and repacking soil into columns most likely stimulated mineralization and nitrification to some degree as it exposed more surface area to soil microbes (Johnson et al., 1995). Johnson et al. (1995) suggested that this effect will be greater in soils with high N such as NDW soils. Additionally, plant uptake, which was not accounted for in the column study, would compete for soil N sources with microbes. Therefore, the laboratory conditions imposed on the soil columns are unlikely to accurately approximate the true conditions occurring in the field. Additional column studies examining different flow rates under controlled conditions. Although results from this study and previous studies on NDW soils (Chapter 6) indicate that the availability of soil N does not limit nitrate production, field conditions such as temperature and moisture very well

may. Therefore, we should expect much lower nitrate concentrations from in situ soil drainage in the NDW.

Base cations

The concentration of the base cations Ca^{2+} and Mg^{2+} in column effluent peaked initially as these cations were displaced from exchange sites by the acidic input. Over time Ca^{2+} and Mg^{2+} continued to be depleted but at a much lower rate. Deposition scenarios 1-4had average depletion rates of 26-30 μmol L^{-1} for Ca^{2+} and 12-13 μmol L^{-1} for Mg^{2+} while scenario 5, which received a relatively high pH influent solution (6.1), had slightly lower depletion rates of 16 μmol L^{-1} for Ca^{2+} and 9 μmol L^{-1} for Mg^{2+} (Table 7-3). The reason for the lower depletion of $Ca^{2+}$and Mg^{2+} in scenario 5 is most likely related to the higher deposition pH in this treatment. A higher pH will increase the number of negatively charged sites on variable-charged soil constituents therefore allowing the soil to hold more exchangeable Ca^{2+} and Mg^{2+}. Sodium was also depleted at all deposition scenarios with the exception of scenario 1, but the high level of sodium added in this treatment was an artifact of the Na_2SO_4 added to the artificial deposition solution in order to attain similar sulfate concentration to natural throughfall. The Na^+ in natural throughfall in the NDW is quite low (17.5 μmol L^{-1}), and therefore the behavior of Na^+ in columns is probably not typical.

Based on the depletion rates measured from our column leaching experiment, the available Ca^{2+} and Mg^{2+} would be fully depleted from the soil within the next 3 to 6 years. However, the depletion rates measured in this experiment may be overestimated because of the large amount of protons added through nitrification as discussed previously. Chapter 3 showed that the depletion rates of Ca^{2+} and Mg^{2+} in the NDW based on 16 years worth of stream data were 10 times lower than our laboratory measured values. Using the field data from the previous study, the estimated

time to depletion is 45 to 70 years. Regardless of which estimate is used, soils in the NDW are clearly base poor with a base saturation below 5% (Chapter 6). Unless depositional pH is significantly increased from its current level of 4.3 (Table 7-3), full watershed recovery may actually be in the order of centuries (Sverdrup et al., 1995).

In contrast to Ca^{2+} and Mg^{2+} behavior in soil columns, K^+ showed a slightly decreasing trend at low PVs followed by an increasing trend with greater PVs (Fig. 7-2). Potassium accumulated in soil columns when inflow K^+ concentration was 37.5-49.1 μmol L^{-1} (scenarios 1-4) but was depleted at low additions of K^+ (9.7 μmol L^{-1}) as in scenario 5. This behavior cannot be readily explained. It is possible that as potassium concentrations are reduced, interlayer K^+ may be released as soil minerals dissolve. If this was occurring to a large extent, however, it would be expected that Al and Si levels would show similar trends. Other processes may be masking Al and Si behavior. Mineral weathering is another mechanism in addition to cation exchange, in which cations can be mobilized. Dahlgren et al. (1990) suggested that the level of dissolved Si can be used as an indicator of mineral weathering. If mineral weathering was a major source of base cations, a significant correlation between the concentrations of base cations and Si would be expected. However, the increasing and then decreasing pattern of effluent Si concentration was distinctly different from that of Ca^{2+}, Mg^{2+} or K^+ (Fig. 7-2). The different patterns seen over increasing PVs suggest that mineral weathering was not significantly contributing to the liberation of base cations in soil columns. Therefore, the depletion of Ca^{2+} and Mg^{2+} was primarily caused by cation exchange.

Metals

All of the studied metals (Al, Cu, Fe, Mn and Zn) were mobilized and depleted from the soil columns although the loss of Cu and Fe was minor (Table 7-2). With a reduced amount of base

Table 7-2 Inflow solution and mean volume-weighted concentration of dissolved elements in soil column leachates in units of μmol L^{-1}, except pH.. The reductions percentages in scenarios 2 to 5 were based on current throughfall deposition loads.

	Through-fall	Scenario 1: current deposition		Scenario 2: 50% S decrease; 48% NO_3^- decrease; 9% NH_4^+ increase		Scenario 3: 90% S decrease; 90% NO_3^- decrease; 40% NH_4^+ decrease		Scenario 4: 90% S decrease; 90% NO_3^- decrease; 80% NH_4^+ decrease		Scenario 5: NDW SW stream water 61% S decrease; 26% NO_3^- decrease; 94% NH_4^+ decrease	
		Influent[a]	Effluent	Influent[a]	Effluent	Influent[a]	Effluent	Influent[a]	Effluent	Influent[a]	Effluent
pH	4.3	4.7	4.5	4.7	4.5	4.7	4.5	4.7	4.5	6.1	4.6
ANC	-48.9	-9.1	-15.2	-8.6	-14.7	-8.5	-15.3	-9.2	-15.1	7.4	-14.8
Cl^-	26.4	115.6	105.7	119.8	126.9	160.7	172.3	152.2	168.0	11.0	22.8
SO_4^{2-}	40.9	56.8	18.5	28.7	16.8	4.9	15.2	4.9	16.7	16.1	20.8
NO_3^-	38.8	58.4	382.6	31.5	332.3	6.9	284.3	6.8	301.5	28.8	355.4
NH_4^+	13.3	17.7	1.4	19.6	0.9	11.1	1.9	4.3	1.2	0.8	0.9
Ca^{2+}	20.4	14.7	41.1	15.2	43.3	13.6	43.1	15.3	45.0	23.0	39.6
Mg^{2+}	7.5	5.4	17.6	5.3	18.5	5.2	17.8	5.2	18.8	9.0	18.3
Na^+	17.5	122.6	108.5	46.6	56.2	29.8	40.4	29.1	39.9	25.5	34.5
K^+	30.7	49.1	31.6	39.0	31.6	40.2	32.6	37.5	32.7	9.7	27.2
Al	2.4	0	36.5	0	38.6	0	41.4	0	42.0	1.1	32.1
Cu	0.1	0	0.1	0	0.1	0	0.1	0	0.1	<DL[b]	0.2
Fe	0.5	0	0.2	0	0.2	0	0.2	0	0.2	<DL[b]	0.3
Mn	1.5	0	7.3	0	7.4	0	8.3	0	8.5	<DL[b]	6.8
Si	3.1	0	94.3	0	91.7	0	91.5	0	94.0	68.5	113.3
Zn	1.3	0	4.0	0	4.3	0	4.4	0	4.4	0.2	3.9

[a] Influent concentrations were based on mean annual volume-weighted throughfall concentration data from 1991 to 2006 (Chapter 3). Concentrations of Al, Cu, Fe, Mn, Si and Zn are from June of 2003 to 2006.
[b] Below detection limit. 0.2, 0.2, and 0.04 μmol L^{-1} for Cu, Fe, and Mn respectively.

cations in soil, hydrolysis of Al and mobilization of other metals will become important mechanisms for neutralizing acid additions. The mobilization of Al is especially important as levels of exchangeable Al in solution as low as 10 μmol L^{-1} are potentially toxic to aquatic organisms (Dahlgren et al., 1990). As acidity increases, more aluminum becomes dissolved as mineral dissolution reactions attempt to buffer decreases in pH. Other authors have suggested that dissolution of Al from organic complexes may also contribute to exchangeable Al in soil solution (Cronan et al., 1986; Mulder et al., 1989), although no attempt was made to measure this fraction in the current study. Dissolved Al concentrations in column effluent from scenarios 1-4 were high (~40 μmol L^{-1}) despite no Al additions. Even at higher influent pH (scenario 5, pH=6.1) exchangeable Al was dissolved from soil columns although the amount was less than from scenarios 1-4. Exchangeable Al was one of the dominant cations, as concentrations of Ca^{2+} in column effluent were similar to levels of dissolved Al in all deposition scenarios.

In contrast to the extensive studies of Al mobilization in soil, few studies have examined the effects of soil acidity on the mobilization of metals (Mannings et al., 1996; Wilson and Bell, 1996; Stevens et al., 2009). In NDW soils, the most important metals in column effluent were Mn and Zn. The dissolution of metals such as Mn and Zn has been reported to be more prevalent in acidic soils than Cu and Fe (Blake et al., 1999; Blake and Goulding, 2002). As the depletion of base cations and the decrease of soil solution pH progresses, the mobilization of metals may play a more important role in consuming added or internally-produced protons via cation exchange. Besides the metals examined in the present study, other metals such as Cd, Co, Cr, Ni and Pb, may also play an important role in acid-impacted soils (Wilson and Bell 1996).

Proton budget

In order to examine the potential biogeochemical sources and sinks of H^+, a proton budget was calculated. Reactions regulating soil water proton concentrations in the column leaching experiment were dominated by nitrification, Al hydrolysis, cations/metals exchange, sulfate adsorption/desorption and mineral weathering (Table 7-3). The amount of protons released or immobilized in all five scenarios was estimated by the equilibrium constants of those major reactions. Nitrification was the main internal source of protons due to the extremely high level of nitrification occurring under laboratory conditions. Mineral weathering reactions mobilizing Si were shown to be the dominant sink for protons and neutralized approximately 60% of total released protons although this is probably an overestimation due to the high levels of Si measured in column effluents. These high Si concentrations are most likely an artifact of the soil sieving that took place before it was packed into columns. This breaking up of large soil aggregates most likely exposed new mineral surfaces and caused an increase in effluent Si that steadily decreased over at higher PVs. Less important but still significant proton sinks were Al dissolution and cation/metal exchange, as each of these reactions consumed about 15% of the total protons. Sulfate was adsorbed causing consumption of protons when influent SO_4^{2-} concentration was greater than 28.7 μmol L^{-1} (scenario 1 & 2), but desorbed causing a release of protons when inflow SO_4^{2-} concentration was less than 20 μmol L^{-1} (scenario 3-5). The amount of protons neutralized by SO_4^{2-} adsorption was significant at high SO_4^{2-} deposition loads as more than 10% of total protons were neutralized by this reaction. Other potential proton sinks, such as neutralization of organic matter, proton accumulation in the soil columns, and exchange reactions involving metals not included here, were not considered in this work but may play important roles in proton consumption (Liu et al., 1990; Dubiková et al., 2002).

Table 7-3. Reactions involved in production and consumption of H^+ and proton budget for each inflow scenario in laboratory soil column experiment. Units are in μmol.

		Scenario 1		Scenario 2		Scenario 3		Scenario 4		Scenario 5	
Reaction processes	Reactions	H^+ source	H^+ sink	H^+ source	H^+ sink	H^+ source	H^+ sink	H^+ source	H^+ sink	H^+ source	H^+ sink
Addition by influent		236		213		237		233		183	
Exported by effluent			391		371		403		381		262
Nitrification	$NH_4^+ + 2O_2 = NO_3^- + H_2O + 2H^+$	7,670		6,391		6,589		6,860		5,982	
SO_4^{2-} adsorption	$Sites(OH)_2^{2-} + SO_4^{2-} + 2H^+ = SitesSO_4^{2-} + 2H_2O$		926		257						
SO_4^{2-} desorption	$SitesSO_4^{2-} + 2H_2O = Sites(OH)_2^{2-} + SO_4^{2-} + 2H^+$					245		272		86	
Al dissolution	$Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O$		1,294		1,235		1,478		1,467		883
Cation/metal exchange[a]	$M\text{-}exch + nH^+ = M^{n+} + nH\text{-}exch$		805		1,136		1,387		1,382		921
Mineral weathering	$SiO_2 + 4H^+ = Si^{4+} + 2H_2O$ $M\text{-}SiO_4 + 4H^+ = H_4SiO_4 + M^{4+}$		4,461		3,909		4,351		4,383		4,149
Sum		**7,906**	**7,877**	**6,603**	**6,907**	**7,071**	**7,618**	**7,365**	**7,613**	**6,251**	**6,214**

[a]M represents base cations and metals (Mn, Zn) accounted for in this study.

Field Lysimeter Study

Column leaching experiments simplify the watershed response to changes in inflow chemistry by neglecting plant uptake, fluctuations in temperature and moisture, heterogeneity of soil and flow divergence. Therefore, results from the column experiment do not fully mimic the natural watershed response to depositional changes. We conducted a field leaching experiment in conjunction with the soil column experiment in order to account for the natural heterogeneity of physical and chemical properties of the soil matrix. Stream water from the NDW was irrigated onto the site to simulate reduced acid deposition. Chemical characteristics of this inflow water are given in Table 7-4. In the field, soil drainage chemistry is dependent on water travel time in soil which is related to pore distribution. In order to evaluate the effect of water throughflow rate to soil drainage chemistry, the leachate samples collected by four pan lysimeters were classified into two groups: fast throughflow samples represented by Lysimeters 1 and 4 with an average collection rate of 1.4 cm day^{-1}, and slow throughflow samples represented by Lysimeters 2 and 3 with an average collection rate of 0.05 cm day^{-1}. The soil effluent chemistry collected from these in situ soil lysimeters was analyzed based on this classification of throughflow rate.

In general, the soil leachate chemistry at a rapid leaching rate was more similar to inflow chemistry, implying that reactions to neutralize protons in soil solution were kinetically limited. The greater magnitude of retention/depletion of chemicals in leachate from slow drainage rates showed that slower water flow increased the chance for interaction between soil solution and the soil solid phase. In this field study, more SO_4^{2-} was exported in leachate solution at slow throughflow rates than at fast water flow. This result indicates that the desorption reaction to mobilize SO_4^{2-} is kinetically limited and that greater desorption will occur given greater reaction time between the solution and solid soil phases. Desorption does not appear to have affected pH

Table 7-4. Mean volume-weighted solution chemistry for inflow solution and soil leachate collected at fast/slow rates from experimental field site. Units are in μmol L^{-1} except for pH.

	Inflow water to experimental site (SW stream water)	Soil leachate at fast collection rate (From Lysimeters 1 & 4)	Soil leachate at slow collection rate (From Lysimeters 2 & 3)
Total collected water amount, cm	220.73	77.29	34.67
Leachate collection rate, cm day^{-1}		1.4	0.05
pH	6.11	5.06	5.74
ANC	6.90	-3.32	5.22
Cl^-	10.55	11.15	11.85
NO_3^-	27.39	21.27	12.28
SO_4^{2-}	16.51	21.97	30.14
NH_4^+	0.64	1.44	1.02
Na^+	25.91	23.91	24.00
K^+	7.31	6.97	12.76
Mg^{2+}	7.14	2.78	2.89
Ca^{2+}	18.86	5.52	5.62
Al	1.46	4.25	1.52
Cu	0.00	0.48	3.76
Fe	0.04	0.10	0.06
Mn	0.00	0.21	1.82
Si	69.66	59.60	39.98
Zn	0.17	0.63	10.23

through the release of protons following ligand exchange of OH^- for SO_4^{2-} which suggests that some other reaction is controlling pH changes.

Nitrate in soil leachate was retained at both slow and fast throughflow rates as opposed to the large release of NO_3^- found in laboratory soil columns. In the field, it was likely that plant uptake and/or microbial assimilation of nitrate were fast enough to consume most or all microbially-produced ammonium and nitrate (Berdén and Nilsson, 1996; Stark and Hart, 1997). Previous studies in the NDW found that approximately 8 kg ha^{-1} yr^{-1}, half of the N deposited in throughfall, accumulated in aboveground biomass (Barker et al., 2002) suggesting that plants in the NDW are able to take up a significant amount of N. At slower throughflow rates of soil solution, more time is allowed for biological reactions to take place, thus accounting for the lower NO_3^- concentrations in lysimeters with slow vs. fast throughflow rates.

In contrast to laboratory soil columns, Ca^{2+} and Mg^{2+} were retained in *in situ* soil at the rate of 70% of inflow Ca^{2+} and 60% of inflow Mg^{2+} (Table 7-4). Additionally, the amount of cation retained was not affected by throughflow rate, indicating that the reaction controlling these cations was not time dependent. Possible retention mechanisms include cation exchange and plant uptake. Potassium was released from the soil at an average rate of 5.45 μmol L^{-1} when throughflow rate was slow, but behaved conservatively at fast flow. This could be due to either plant uptake or, more likely, exchange reactions in which K^+ is released into solution when another cation takes its place on exchange sites.

Aluminum in soil leachate exhibited the opposite behavior of all other studied chemicals with changes in throughflow rates. Significantly more exchangeable Al was exported from the soil during fast throughflow compared to slow throughflow although the magnitude of difference is less than 3 μmol L^{-1}. Because faster water flow through soils allows for less interaction between

solution and solid phases and the kinetic limitations on the dissolution of Al, it is likely that the higher concentration of Al in leachate was from exchange sites or from the dissolution of Al (Clayton et al., 1991a; Dahlgren and Walker, 1993). At low levels of base cations and pH, Al may be expected to be held on cation exchange sites where it could be exchanged and released into solution at fast flow rates. Dissolution of Al may be another source of Al export in this case. The kinetically unlimited dissolution of Al was inversely correlated with solution pH (Matzner et al.1998). The lower solution pH found in lysimeters which had faster drainage rates enhanced the dissolution of Al mineral to increase the export of dissolved Al. The simultaneous reactions of cation exchange and mineral dissolution at faster throughfall increased the amount of dissolved Al to be drained from soil. The concentrations of the metals Cu, Zn and Mn in leachate solutions were greater in lysimeters draining slowly compared to those draining faster. Slower throughflow allows greater reaction time for mineral weathering to take place compared to fast throughflow.

The travel time of water passing through soil controlled the amount of solute retention or depletion in the NDW and the time pattern of soluble contaminants (Kirchner et al., 2000). Soil is spatially heterogeneous, reflected by the diversity of flow paths. Describing flow paths is essential to being able to predict the transport of soluble chemicals. With slow throughflow, chemicals were transported through the soil matrix primarily by convection/dispersion. In contrast, fast throughflow was probably due to preferential macropore flow and allowed for enhanced solute transport of most chemicals (Buttle and Leigh, 1997). The bypass of water during fast throughflow minimized the reactions between solutes and the solid phase, resulting in less change to soil solution chemistry than during slow throughflow. In nature, fast and slow throughflow most likely exist simultaneously due to soil heterogeneity. Yet watershed models

fail to account for this diversity despite the strong impact of flow paths on solution chemistry. A complete understanding of the dynamics between soil solution chemistry and hydrology is sorely lacking and additional studies examining differing rates of soil water flow under both field and controlled conditions are needed.

SUMMARY AND CONCLUSIONS

The 4-month laboratory and field soil leaching experiments conducted in the NDW indicated that the recovery of the watershed should be determined by deposition loads and flow rate. Fast flow exported added chemicals rapidly but minimized the kinetically controlled reactions between soil and water and extended the time required for watershed recovery. Deposition loads of SO_4^{2-} and H^+ were the most important parameters controlling watershed recovery. Recovery of the watershed as represented by retention of Ca^{2+} and Mg^{2+} pools occurred when sulfur deposition loads were reduced by 60% of the current deposition amount. This process can be enhanced with an increase of deposition pH. At current acid deposition loads mineral weathering, dissolution of Al, cation exchange of Ca^{2+} and Mg^{2+} and adsorption of SO_4^{2-} were the major mechanisms in neutralizing additions of strong acid. Following the reduction of the Ca^{2+} and Mg^{2+} pools in soil, release of K^+ and metals such as Mn and Zn became more important for neutralizing acid. This soil leaching experiment might provide insight into future developments of watershed acidification in forest ecosystems responding to reductions of SO_2, NOx and NH_3 emissions.

CHAPTER 8 SUMMARY AND FUTURE WORK

This chapter summarizes the accomplishments of this study and recommendations for future research.

SUMMARY

Stream acidification in the NDW was controlled by acid deposition, and regulated by climate change and internal biogeochemical processes (Fig. 8-1). Atmospheric deposition of sulfur and nitrogen were the primary driver for surface water and soil acidification. However, plant uptake of nitrogen, soil adsorption of sulfate, cation exchange of base cations, and hydrolysis of Al can reduce the amount of acidity exported into streams. Due to the long-term addition of acidity by atmospheric deposition and internal nitrification process, the release of base cation and Al reduced the base reservoir and increased the toxic Al ions. The reduction of base reservoir weakened the soil buffer capacity to future acid deposition and may delay the watershed recovery. Hydrologic changes, such as stormflow may enhance the stream acidification.

The NDW has received long-term acid deposition with high loadings of sulfur and nitrogen. The throughfall deposition load of sulfate was 1,735 eq ha^{-1} yr^{-1}. On average, 61% of deposited sulfate was accumulated in soil based on annual net flux, resulting in an exchangeable SO_4^{2-} content in soil was around 203 to 235 μeq kg^{-1}. Reduction of soil solution pH or organic matter may enhance the adsorption of sulfate elevating this net retention percentage. Sulfate adsorption is a dominant geochemical process in the soil that neutralizes protons. As estimated from soil leaching experiment, around 10% of protons were consumed by this process. However, sulfate desorption can release protons and acidify soil and water. Because of this process and resulting

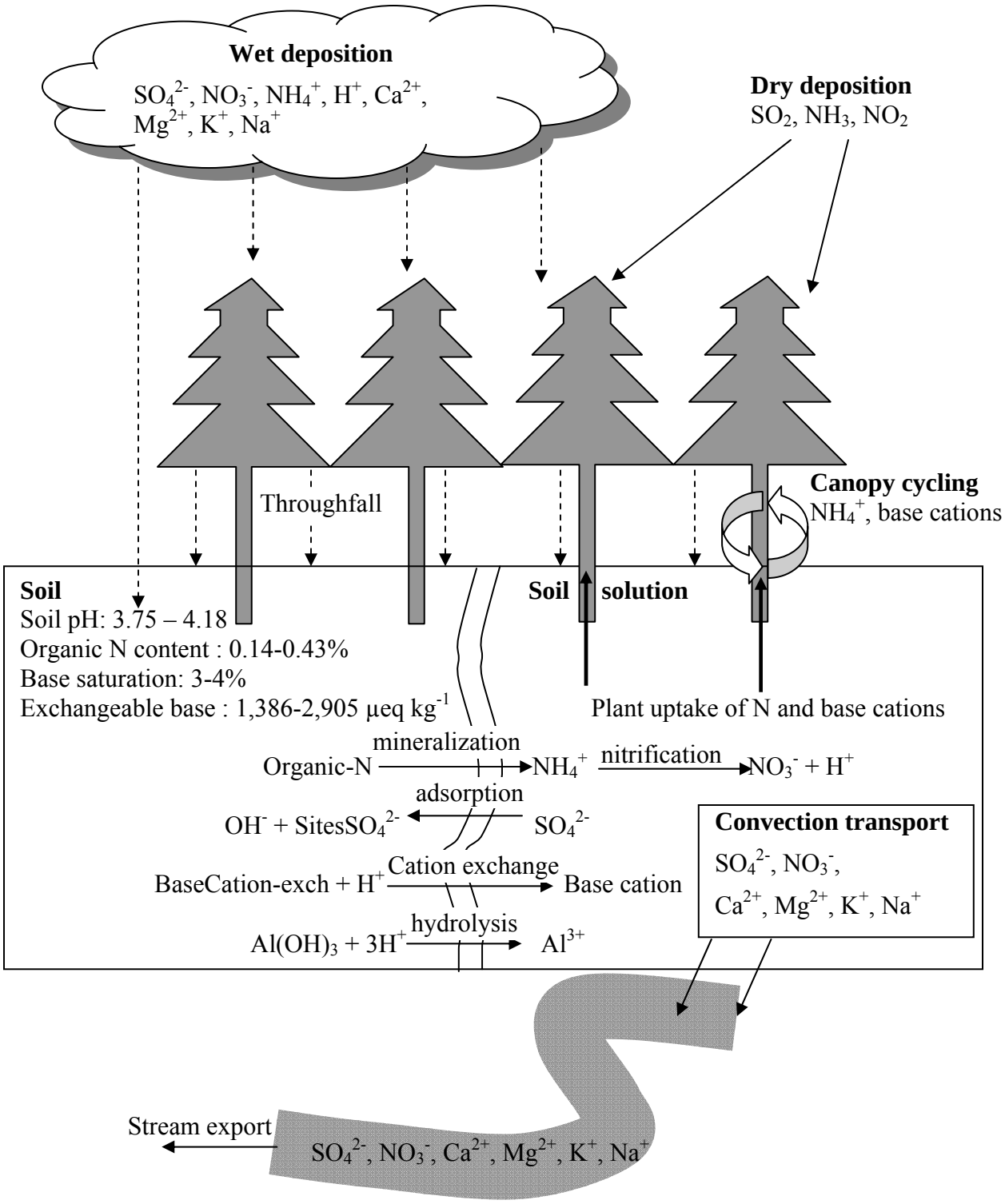

Fig. 8-1. A conceptual model to present the watershed acidification from deposition to vegetation and soil process, and stream export in the NDW. Biogeochemical processes are a function of climate and precipitation volumes per time.

acidification, watershed recovery could be delayed even though desorption of sulfate actually occurred in future.

Nitrogen from atmospheric deposition was added into the NDW largely in form of NO_3^- (863 eq ha^{-1} yr^{-1}) and NH_4^+ (284 eq ha^{-1} yr^{-1}). Around 32% of deposition inorganic nitrogen was retained in the NDW, mainly by forest uptake. Owing to the recovery of forest from the dieback caused by balsam woolly adelgid, the retention amount of inorganic nitrogen was increasing at the rate of 44.30 eq ha^{-1} yr^{-1}. Biological conversion of nitrogen, particular nitrification, was the dominant process to produce protons internally. This reaction was especially significant in upper soil horizon, as nitrate concentration was increased from 38.8 μeq L^{-1} in throughfall to 126.9 μeq L^{-1} in A horizon and the pH was reduced from 4.3 in throughfall to 4.0 in A horizon. In soil, organic nitrogen content was 500 times greater than inorganic nitrogen. The unlimited supply of nitrogen source implied that the export of nitrogen was controlled by internal processes rather than by deposition.

Because of long-term acid deposition and internally produced acidity, acidification of streams in the NDW was significant because the average stream ANCs were below 10 μeq L^{-1} and pHs were between 5.5 to 5.8. The acidification in surface water was especially significant during storm-event when stream ANC and pH dropped by 4 μeq L^{-1} and 0.2 pH unit averagely. The episodic increase of stream acidity may be attributed to the elevation of sulfate concentration during stormflow, because short retention time during storm event minimized soil adsorption of sulfate so that to export more sulfate.

Besides streams, soil was also acidified as evidenced by low base saturation, which had average values of 3% to 4% for soils in A, Bw and Cb horizons. This low base saturation was caused by continuously depletion of Ca^{2+}, Mg^{2+} and Na^+, which were leached from the NDW at

the rates of 77, 46 and 66 eq ha^{-1} yr^{-1}, respectively. At current depletion rates, soil pool of Ca^{2+} and Mg^{2+} was estimated to be empty in next 45 to 70 years. Because of the reduction of base pool, hydrolysis of Al was becoming the dominant process in soil that neutralizes protons. Exchangeable Al has accounted for over 56% of the exchangeable acidity. The limited supply of base cations and mobilization of aluminum in soil may affect the forest productivity and growth.

Potential changes of soil and water chemistry investigated in this study provided essential information on the deterioration of acid deposition to high-elevation ecosystem. This data can help improve natural resource managers to better understand watershed acidification processes, and manage accordingly. Results may be used for the development of biogeochemical models in order to predict the response of high-elevation watersheds to future changes in acid deposition.

FUTURE RESEARCH

Future research in the NDW is recommended to support development of a biogeochemical model for the prediction of stream acidification, and estimation of deposition critical loads for S and N. Findings in current research and from model simulations can be employed to compare with other high-elevation watersheds in the United States to investigate the effects of watershed characteristics to soil and water chemistry.

The long-term monitoring in the NDW provided appreciable data to evaluate the impacts of acid deposition to terrestrial system. Continued monitoring of water chemistry in this site is highly recommended as few sites in North America, especially in southern Appalachians, have such a complete, long-term monitoring program.

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Vita

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